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Approximate self-consistent field calculations of molecular potential surfaces

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APPROXIMATE SELF-CONSISTENT FIELD CALCULATIONS OF MOLECULAR POTENTIAL SURFACES

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APPROXIMATE

SELF-CONSISTENT FIELD CALCULATIONS

OF MOLECULAR POTENTIAL SURFACES

by

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ABSTRACT

The Approximate Self-Consistent Field Molecular Orbital Theory
(ASCFT) with complete neglect of differential overlap (CNDO) has been
applied to the calculation of electronic structure for several selected
molecules in this text. The theory leads to calculated equilibrium
geometry configurations and the barrier to internal rotation of ethane,
inversion barrier of ammonia and the barrier for cis to trans conversion
for difluorodiazine. These results are in reasonable agreement with
experimental values in most cases. The stretching force constants are
higher than experimental values by a factor of approximately two. The
orbital energy levels for ammonia and for oxygen difluoride as a function
of bond angles were in reasonable agreement with the full LCAO-SCF
Calculations. A variation of parameters to find a new set of parameters
was attempted with unsuccessful results.

The Extended Hückel Theory (EHT) can be applied to aliphatic
hydrocarbons but its application to non-hydrocarbon molecules is quite
limited.

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I. INTRODUCTION

There are many levels of sophistication for the calculation of electronic structure using molecular orbital methods. The simplest approach is the Hückel Molecular Orbital Theory (HMO). This is one of the semiempirical methods which is used extensively in the quantum mechanical study of the mobile electrons of conjugated molecules. The HMO was extended by many people. One of the theories examined in this paper is the "Extended Hückel Theory (EHT)" which was developed by Roald Hoffmann (1). A higher level of sophistication is the self-consistent field (SCF) molecular orbital calculation. One of those methods which has recently been developed is based on a theory introduced by J. A. Pople: "Approximate Self-Consistent Field Molecular Orbital Theory (ASCFT)" (2), (3), (4). This ASCFT Calculation is predominantly used throughout this text.

We can say molecular orbital methods are "curve fitting". They are really based on semiempirical methods. The purposes of the calculation described herein are the prediction of potential surface by Pople's theory to examine and to try to improve the agreement of a calculated potential surface with an experimental potential surface.

The background describing each of these theories will be discussed in the next section.

II. Hückel Molecular Orbital Theory (HMO)

In this theory, the mobile electrons can be treated as occupying a set of delocalized molecular orbitals (by the Pauli Exclusion Principle, not more than two electrons in each molecular orbital). These molecular

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orbitals are eigenfunctions of a one electron Hamiltonian. The orbitals are approximated by a linear combination of atomic orbitals (LCAO) centered on various atoms. The Slater type atomic orbitals (5) are generally used as approximations to the actual atomic orbitals for each atom. When this theory is applied to a wide range of molecules, it has the advantage of great simplicity but serious discrepancies result because of the neglect of interelectronic repulsions for the case of many electrons.

For the unsaturated molecules: The π - molecular orbitals are formed by a LCAO of the $2P_z$ atomic orbitals which, it is assumed, share the same nodal plane. In N-π electron systems, the molecular orbitals are given by

$$\Psi_j = \sum_{\nu=1}^{N} C_{j\nu}\, \phi_\nu$$
$$(j = 1, \cdots, N) \tag{1.1}$$

where Ψ_j represents the jth molecular orbital, ϕ_ν represents the atomic orbital in the νth atom and $C_{j\nu}$ represents the coefficients of the jth molecular orbital and the νth atom (atomic orbital). It is noted that the subscript i, j, k, l etc. stand for the molecular orbitals and $\mu, \nu, \sigma, \lambda$ etc. stand for the atoms or atomic orbitals.

From a given electron Hamiltonian, Equation (1.1) must satisfy the equation

$$\mathcal{H}\Psi_j = E_j \Psi_j \tag{1.2}$$

Where Ej is the eigenvalue of the jth state, Ψ_j is a column matrix, and $\mathcal{H}$ is the Hamiltonian operator. This can be put in matrix form:

$$(\mathcal{H})\begin{pmatrix} \psi_1 \\ \vdots \\ \psi_N \end{pmatrix} = \begin{pmatrix} E_1 & 0 & - & - & - & 0 \\ 0 & E_2 & & & & \vdots \\ \vdots & & 0 & & & 0 \\ \vdots & & & 0 & & \vdots \\ 0 & - & - & - & 0 & E_N \end{pmatrix}\begin{pmatrix} \psi_1 \\ \vdots \\ \psi_N \end{pmatrix} \tag{1.2'}$$

We multiply equation (1.2) by ψ_i^* and integrate over all space, $d\tau$, then we obtain

$$\int \psi_i^* \mathcal{H} \psi_j \, d\tau = \int \psi_i^* E_j \psi_j \, d\tau \tag{1.3}$$

Substituting equation (1.1) into (1.3)

$$\sum_\mu \sum_\nu C_{i\mu}^* C_{j\nu} \int \phi_\mu^* \mathcal{H} \phi_\nu \, d\tau = \sum_\mu \sum_\nu C_{i\mu}^* C_{j\nu} E_j \int \phi_\mu^* \phi_\nu \, d\tau \tag{1.4}$$

Defining

$$H_{\mu\nu} = \int \phi_\mu^* \mathcal{H} \phi_\nu \, d\tau \tag{1.5}$$

and

$$S_{\mu\nu} = \int \phi_\mu^* \phi_\nu \, d\tau \tag{1.6}$$

We may write equation (1.4)

$$\sum_{\mu,\nu} C_{i\mu} C_{j\nu} H_{\mu\nu} = E_j \sum_{\mu,\nu} C_{i\mu} C_{j\nu} S_{\mu\nu} \tag{1.7}$$

Taking the derivative of equation (1.7) with respect to $C_{k\lambda}$ to minimize the energy $\left(\partial E_j / \partial C_{k\lambda} = 0 \right)$, we obtain

$$\sum_\mu C_{k\mu} H_{\mu\lambda} + \sum_\nu C_{k\nu} H_{\lambda\nu} = E_k \left(\sum_\mu C_{k\mu} S_{\mu\lambda} + \sum_\nu C_{k\nu} S_{\lambda\nu} \right) \tag{1.8}$$

It may be shown that

$$S_{\mu\nu} = S_{\nu\mu} \tag{1.9}$$

$$H_{\mu\nu} = H_{\nu\mu} \tag{1.10}$$

Therefore we obtain the equation

$$\sum_\mu C_{k\mu} H_{\mu\lambda} = E_k \sum_\mu C_{k\mu} S_{\mu\lambda} \tag{1.11}$$

or

$$\sum_\mu C_{k\mu} \left(H_{\mu\lambda} - E_k S_{\mu\lambda} \right) = 0 \tag{1.12}$$

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This equation (1.12) is the well-known secular equation and gives rise to the secular determinant:

$$| \, H_{\mu\lambda} - E_k S_{\mu\lambda} \, | = 0 \tag{1.13}$$

Equation (1.13) is the non-trivial solution of (1.12).

Now we discuss the Hermitian Property of the Matrices $(H_{\mu\lambda})$ and $(S_{\mu\lambda})$. A matrix H is said to be Hermitian if it is equal to the conjugate of its transpose, i.e.,

$$\overline{H'} = H$$

$$\text{Where} \quad H = (H_{\mu\lambda}) \quad \text{and} \quad \overline{H'} = (\overline{H_{\lambda\mu}}) \tag{1.14}$$

$$(\mu, \lambda = 1, 2, \cdots, N)$$

By definition, a real Hermitian matrix is symmetric, but an imaginary symmetric matrix is not necessarily an Hermitian matrix. It is noted that the eigenvalues of an Hermitian matrix are all real.

Next we discuss some transformation properties. In general, the atomic orbital ϕ_ν does not form a complete orthonormal set. This basis, ϕ_ν, can be transformed into an orthonormal basis by using a unitary transformation matrix such that

$$\phi_\nu^{new} = \sum_\lambda T_{\nu\lambda} \, \phi_\lambda^{old} \tag{1.15}$$

where ϕ_ν^{new} is the new orthonormal basis formed by transforming the old basis ϕ_λ^{old} in N dimensional space and $T_{\nu\lambda}$ is the transformation matrix element. The old H can also be transformed into a new basis such that

$$H_{\mu\nu}^{new} = \sum_{\lambda,\sigma} T_{\mu\sigma}^* T_{\nu\lambda} \int \phi_\sigma^* \mathcal{H} \phi_\lambda \, d\tau \tag{1.16}$$

It may be recalled that the old basis is $H_{\sigma\lambda}^{old} = \int \phi_\sigma^* \mathcal{H} \phi_\lambda \, d\tau$.

Therefore equation (1.16) can be rewritten

$$H_{\mu\nu}^{new} = \sum_{\sigma,\lambda} T_{\mu\sigma}^* H_{\sigma\lambda}^{old} T_{\nu\lambda} \tag{1.16}'$$

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or

$$H_{\mu\nu}^{new} = \sum_{\sigma,\lambda} T_{\mu\sigma}^* H_{\sigma\lambda}^{old} T_{\lambda\nu}' \tag{1.17}$$

It is noted that if the transformations were made:

$$\phi_{\nu}^{new} = \sum_{\lambda} \phi_{\lambda} T_{\lambda\nu} \tag{1.18}$$

then the equation (1.17) becomes

$$H_{\mu\nu}^{new} = \sum_{\sigma,\lambda} T_{\mu\sigma}^{*'} H_{\sigma\lambda}^{old} T_{\lambda\nu} \tag{1.19}$$

Equations (1.17) and (1.19) can be written by matrix notation such that

$$H^{new} = T^* H^{old} T' \tag{1.17'}$$

and

$$H^{new} = T^{*'} H^{old} T \tag{1.19'}$$

From equation (1.19)', if T is a unitary matrix $\left(T^{-1} = T^{*'}\right)$ then we have

$$H^{new} = T^{-1} H^{old} T \tag{1.20}$$

This equation (1.20) is frequently used and usually T is real and H^{old} is a symmetric matrix.

Referring to the secular equation (1.12), we define $\lambda_{kk} = E_k$, then

$$\sum_{\mu} \left(H_{\lambda\mu} C_{\mu k} - S_{\lambda\mu} C_{\mu k} \lambda_{kk} \right) = 0 \tag{1.21}$$

This can be expressed in matrix notation in the following manner

$$HC - SC\lambda = 0 \tag{1.21'}$$

where
$$H = (H_{\lambda\mu}) \qquad \lambda = (\lambda_{kk})$$
$$C = (C_{\mu k})$$
$$S = (S_{\lambda\mu}) \qquad (\lambda, \mu, k = 1, \cdots N)$$

Therefore, we obtain

$$\lambda = (\lambda_{kk}) = C^{-1}(S^{-1}H)C \tag{1.22}$$

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It is generally true that the matrix $(S^{-1}H)$ may not be symmetric. In equation (1.22), the eigenvalue cannot be obtained by methods usually employed to diagonalize Hermitian matrices. One way to solve this problem is to transform the matrix S to an orthonormal basis, then diagonalize the H matrix. The procedures are described as follows: Using the transformation matrix Q such that $\psi = Q\phi$, we transform the matrix S to the identity matrix I

$$S^{new} = I = Q S^{old} Q'$$

(1.23)

or

$$S^{old} = (Q'Q)^{-1}$$

(1.24)

Also we diagonalize the matrix S by a unitary transformation matrix T such that

$$\lambda = T S^{old} T'$$

(1.25)

or

$$S^{old} = (T'\lambda^{-1}T)^{-1}$$
$$= \left[(T'\lambda^{-\frac{1}{2}}T)'(T'\lambda^{-\frac{1}{2}}T) \right]^{-1}$$

(1.26)

Equating equation (1.24) and (1.26), we obtain

$$Q = T'\lambda^{-\frac{1}{2}}T$$

(1.27)

Then we transform the old basis H to the new basis by the transformation matrix Q such that

$$H^{new} = Q H^{old} Q'$$
$$= (T'\lambda^{-\frac{1}{2}}T)(H^{old})(T'\lambda^{-\frac{1}{2}}T)'$$

(1.28)

Finally we can diagonalize H^{new} by the matrix U. Then we obtain the eigenvalues

$$E = U H^{new} U'$$
$$= (UT'\lambda^{-\frac{1}{2}}T)(H^{old})(UT'\lambda^{-\frac{1}{2}}T)'$$

(1.29)

where U is the matrix which diagonalizes the H^{new} and T is the unitary

matrix which diagonalizes S. Also the correct eigenfunctions are

$$\Psi = UT'\lambda^{-\frac{1}{2}}T\phi \qquad (1.30)$$

The general operations for the application of HMO theory to

specific problems are

(a) Setting up the Secular determinant

(b) Expanding the Secular determinant

(c) Finding the eigenvalues

(d) Determining the M.O.'s by finding the eigenvectors.

III. Extended Hückel Theory (EHT)

Hückel calculations originally were applied exclusively for the

Planar conjugated and aromatic systems of π electrons with the neglect

of overlap for non-adjacent atoms. In the extended Hückel theory (EHT),

Roald Hoffmann (1) expanded the basis set to consist of 2s and 2P

orbitals for Carbon atoms and 1s orbitals for Hydrogen, with the

inclusion of all overlap integrals. The EHT can calculate molecular

orbitals for the aliphatic and aromatic compounds which gives good

results for most hydrocarbons because of the resonable set of parameters

chosen for the calculations. The parameters are nicely adjusted to the

self-consistent value for the hydrocarbons but when the EHT is applied

to non-hydrocarbons, it is not as successful, and even predicts a lack

of minima in many bond stretching motions.

III-A. Method of Calculation

For the calculation of the molecule CnHm, we use a basis set

consisting of m-Hydrogen Slater orbitals, n-2s and 3n-2P orbitals.
The Slater exponents were selected to be 1.0 for Hydrogen and 1.625
for Carbon throughout the calculations. It is noted that 1.20 was
selected for Hydrogen in the calculation of the ethane molecule. Those
values are listed in Table 1. The order of the matrix is 4n + m which
gives the number of energy levels of the system and the eigenvalue E's
for off diagonal matrix elements are retained in the Secular Equation.

TABLE 1

Slater exponents for valence Shell S and P atomic orbitals.

H	1.0*	C^-	1.45	O^-	2.10
Li	0.65	C	1.625	O	2.275
Be	0.975	C^+	1.80	O^+	2.45
B^-	1.125	N	1.95	F	2.60
B	1.30	N^+	2.125		

* Present calculations we carried out using 1.2 for Hydrogen.

The diagonal elements $H_{\mu\mu}$ are chosen to be valence state ionization
potentials; the particular values used are essentially those of Skinner
and Pritchard (6). For example, the SP^3 valence state ionization
potentials for Carbon and 1s Hydrogen atoms have the following values:

$$H_{\mu\mu}(C_{2p}) = -11.4 \quad e.v.$$

$$H_{\mu\mu}(C_{2s}) = -21.4 \quad e.v. \tag{2.1}$$

$$H_{\mu\mu}(H_s) = -13.6 \quad e.v.$$

The choice of the off-diagonal term $H_{\mu\nu}$ is approximated as

$$H_{\mu z} = 0.5 \, K \, (H_{\mu \mu} + H_{zz}) \, (S_{\mu z})$$

<div align="right">(2.2)</div>

The approximation (2.2) was first discussed by Mülliken (7) and used
in the M.O. Calculations by Wolfsberg and Helmholtz (8).

The value of K in equation (2.2) was chosen to be 1.75. These
calculations give gairly good results for hydrocarbons.

IV. Approximate Self-Consistent Field Molecular Orbital Theory (ASCFT)

Approximate methods for obtaining self-consistent field molecular
orbitals have recently been developed by J. A. Pople (2), (3), (4).
Slater type orbitals (5) are used as basis functions. Overlap integrals
between two different atoms were calculated using the formula given by
Mülliken, Rieke, Orloff and Orloff (9). It is assumed that the Slater
type atomic orbitals are real atomic orbitals, and that the M.O.'s for
the ground state are obtained by Linear Combinations of Slater type
atomic orbitals. If the Coefficients in the LCAO Molecular orbitals
are chosen to minimize the total energy, one obtains LCAO - SCF orbitals.
The best LCAO approximation to SCF functions were first given by Roothaan
(10). It is noted that the EHT treated all the electrons independently.
EHT wave functions are used as a starting point for the self-consistent
field interations in this ASCFT.

The SCF methods were developed using two approximations based on
the neglect of the differential overlap between all valence atomic
orbitals. One of these involves complete neglect of differential overlap
(CNDO) in all basis sets connected by the transformations as mentioned
in Section I, that is: the off-diagonal elements of overlap matrix
in the Hamiltonian matrix are to be neglected. The other involves the

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neglect of the products of $\phi_\mu(1)\phi_\nu(1)$ of any two atomic orbitals ϕ_μ and ϕ_ν in all electron-repulsion integrals. This complete neglect of differential overlap of all basis sets will result in non-orthonormal basis sets.

The CNDO method in ASCFT should be regarded as an approximation to a full LCAO - SCF calculation which uses a minimal basis containing only inner-shell and valence-shell atomic orbitals. The Slater exponents used in these calculations are listed in Table 1 (for Hydrogen, 1.2 is used). The values for β° and ionization potentials in 2s and 2p atomic orbitals from Lithium to Fluorine were set semiempirically. Those values used in these calculations are tabulated in Table 2 and Table 3 respectively.

TABLE 2

Bonding Parameters β_A° (in e.v.)

Atom	H	Li	Be	B	C	N	O	F
	9	9	13	17	21	25	31	39

TABLE 3

"Average" Ionization Potentials I_μ (in. e.v.)

Atom	H	Li	Be	B	C	N	O	F
1s	13.06	--	--	--	--	--	--	--
2s	--	5.39	9.32	14.05	19.44	25.58	32.38	40.20
2P	--	3.54	5.96	8.30	10.67	13.19	15.85	18.66

The CNDO method of ASCFT can be used for closed ground shell structures and doublets, but a triplet structure is not available with the computer program used (for example O_2, B_2 and C_2). The computer program is presented in Appendix 1.

IV-1. Self-Consistent Field (SCF) Equation

The initial discussion covers Roothann's LCAO - SCF method (10) as a basis for calculating the MO's of a molecule, paying particular attention to transformation properties. The Is Hydrogen and valence shell electrons for Li to F are assigned to LCAO molecular orbitals. Minimization of total energy by a variation principle with SCF orbitals leads to a series of simultaneous non-Linear equations, the so called Hartree Fock equations (11), which are applied to LCAO molecular orbitals with a closed shell configuration. These equations were shown by Roothaan to reduce to the form (10)

$$\sum_{\nu} F_{\mu\nu} C_{\nu i} = \sum_{\nu} S_{\mu\nu} C_{\nu i} \epsilon_i \tag{4.1}$$

where (using atomic units)

$$F_{\mu\nu} = H_{\mu\nu} + G_{\mu\nu} \tag{4.2}$$

$$H_{\mu\nu} = \int \phi_\mu^* \left(-\frac{1}{2}\nabla^2 - \sum_A V_A(r) \right) \phi_\nu \, d\tau \tag{4.3}$$

$$G_{\mu\nu} = \sum_{\lambda,\sigma} P_{\lambda\sigma} \left[(\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\sigma|\nu\lambda) \right] \tag{4.4}$$

$$(\mu\nu|\lambda\sigma) = \iint \phi_\mu^*(1) \phi_\nu(1) \frac{1}{r_{12}} \phi_\lambda^*(2) \phi_\sigma(2) \, d\tau_1 \, d\tau_2 \tag{4.5}$$

$$S_{\mu\nu} = \int \phi_\mu^* \, \phi_\nu \, d\tau \tag{4.6}$$

$$P_{\lambda\sigma} = 2 \sum_i^{occ} C_{i\lambda}^* \, C_{i\sigma} \tag{4.7}$$

Where Ei is the orbital energy for the ith M.O. $H_{\mu\nu}$ is the matrix element of the one electron Hamiltonian including the kinetic energy and the Potential energy in the electrostatic field of the core, this being written as a sum of potentials $V_A(r)$ for various atoms A in the molecule. $G_{\mu\nu}$ is the matrix element of the potential due to valence electrons and depends on the M.O.'s via the population matrix $P_{\lambda\sigma}$.

The total energy of the molecule is obtained by adding the repulsion energy between isolated cores and the separated valence electrons. The repulsion term can be approximated by a point charge model

$$E_{total} = E_{electronic} + \sum_{A<B} \sum Z_A Z_B / R_{AB} \tag{4.8}$$

where Z_A is the core charge of atom A. The electronic energy is given by

$$E_{operator} = 2 \sum_i H_i + \sum_{i,j} (2 J_{ij} - K_{ij}) \tag{4.9}$$

$$E_{electronic} = 2 \sum_{\mu,\nu,i} C_{\mu i} C_{\nu i} H_{\mu\nu} + \sum_{\mu,\nu,i} C_{\mu i} C_{\nu i} G_{\mu\nu}$$

$$= \sum_{\mu,\nu} P_{\mu\nu} H_{\mu\nu} + \frac{1}{2} \sum_{\mu,\nu} P_{\mu\nu} G_{\mu\nu}$$

$$E_{elect.} = \frac{1}{2} \sum_{\mu,\nu} P_{\mu\nu} \left[2 H_{\mu\nu} + G_{\mu\nu} \right]$$

$$= \frac{1}{2} \sum_{\mu,\nu} P_{\mu\nu} \left[H_{\mu\nu} + F_{\mu\nu} \right] \qquad (4.10)$$

IV-2. Theory with Complete Neglect of Differential Overlap (CNDO)

First consider the simplest version of the theory which involves the complete neglect of differential overlap between atomic orbitals on the same atom. The approximations are given below.

Approximation A

The atomic orbitals ϕ_μ are treated as if they form an orthonormal set such that $S_{\mu\nu} = \delta_{\mu\nu}$ and then the $C_{i\mu}$ forms an orthonormal matrix. The condition for orthonormality becomes:

$$\sum_\mu C_{i\mu} C_{j\mu} = \delta_{ij} \qquad (4.11)$$

With this approximation, the diagonal matrix elements $P_{\mu\mu}$ (electron density) correspond to the electron populations of the atomic orbitals ϕ_μ and

$$\sum_\mu P_{\mu\mu} = 2N \qquad (4.12)$$

where 2N is the number of valence electrons.

Approximation B.

Equations (4.4) are neglected because of the orthonormality of atomic orbitals. This means $(\mu\nu | \lambda\sigma)$ is zero unless $\mu = \nu$ and $\lambda = \sigma$. The non-zero values will be written $\gamma_{\lambda\mu}$ such that

$$\gamma_{\lambda\mu} = \left(\lambda\lambda \,\middle|\, \mu\mu \right)$$

(4.13)

Approximation C

The electron-interaction integrals $\gamma_{\mu\nu}$ are assumed to depend only on the atoms to which the orbitals ϕ_μ and ϕ_ν belong and not on the actual type of the orbitals. This means that there remains only a set of atomic electron-interaction integrals γ_{AB} measuring an average repulsion between an electron in valence atomic orbital on atom A and another in a valence orbital on atom B. The set of atomic orbitals on one particular atom A is replaced by an alternative set tm,

$$t_m = \sum_\mu O_{m\mu}\, \phi_\mu$$

(4.14)

A general electron-replusion integral in this new basis set is given by

$$\left(t_m t_n \,\middle|\, \phi_\lambda \phi_\lambda \right) = \sum_\mu O_{m\mu} O_{n\mu} \left(\phi_\mu \phi_\mu \,\middle|\, \phi_\lambda \phi_\lambda \right)$$

(4.15)

Now we apply approximation C, then equation (4.15) becomes

$$\left(t_m t_n \,\middle|\, \phi_\lambda \phi_\lambda \right) = \gamma_{AB}\, \delta_{mn}$$

(4.16)

It is noted that equation (4.16) is invariant under the orthogonal transformation matrix **O** which gives the new basis **t**.

Using approximation A, and B, the matrix elements $F_{\mu\nu}$ become

$$
\begin{aligned}
F_{\mu\mu} &= H_{\mu\mu} + G_{\mu\mu} \\
&= H_{\mu\mu} + \sum_{\lambda,\sigma} P_{\lambda\sigma}\left[(\mu\mu|\lambda\sigma) - \tfrac{1}{2}(\mu\sigma|\mu\lambda) \right] \\
&= H_{\mu\mu} - \tfrac{1}{2} P_{\mu\mu}\, \gamma_{\mu\mu} + \sum_{\sigma(\neq\mu)} P_{\sigma\sigma}\, \gamma_{\mu\sigma}
\end{aligned}
$$

(4.17)

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$$F_{\mu\nu} = H_{\mu\nu} - \frac{1}{2} P_{\mu\nu} \gamma_{\mu\nu} \tag{4.18}$$

Equation (4.17) and (4.18) can be rewritten by approximation C

$$F_{\mu\mu} = H_{\mu\mu} - \frac{1}{2} P_{\mu\mu} \gamma_{AA} + P_{AA} \gamma_{AA} + \sum_{(B \neq A)} P_{BB} \gamma_{AB} \tag{4.19}$$

$$F_{\mu\nu} = H_{\mu\nu} - \frac{1}{2} P_{\mu\nu} \gamma_{AB} \tag{4.20}$$

where μ belongs to atom A and P_{BB} is the total valence electron density on atom B.

$$P_{BB} = \sum_{\nu}^{B} P_{\nu\nu} \tag{4.21}$$

Also the core matrix $H_{\mu\mu}$ can be separated as follows:

$$H_{\mu\mu} = \left(\mu \left| -\frac{1}{2} \nabla^2 - V_A \right| \mu \right) - \sum_{B(\neq A)} \left(\mu \left| V_B \right| \mu \right)$$

$$= U_{\mu\mu} - \sum_{B(\neq A)} \left(\mu \left| V_B \right| \mu \right) \tag{4.22}$$

$$H_{\mu\nu} = U_{\mu\nu} - \sum_{B(\neq A)} \left(\mu \left| V_B \right| \nu \right)_{(\mu \neq \nu)} \tag{4.23}$$

where $U_{\mu\mu}$ is the diagonal element of ϕ_μ with respect to the one-electron Hamiltonian containing only the core of its own atom ($U_{\mu\mu}$ is an atomic quantity measuring the energy of the atomic orbital) and $U_{\mu\nu}$ is the one-electron matrix element using the local core Hamiltonian (μ and ν are on the

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same atoms). It is noted that the cores consist of the nucleus and
inner-shell electron.

Approximation D

The interaction terms of the distribution $\phi_\mu \phi_\nu$ on atom A
and the nucleus of atom B, $(\mu | V_B | \nu)$ are equal to zero if $\mu \neq \nu$.
The integrals $(\mu | V_B | \nu)$ are taken to be the same for all valence
atomic orbitals on Atom A and there results

$$V_{AB} = \left(\mu | V_B | \mu \right)$$

(4.24)

It should be noted that the attraction term matrix element V_{AB}
between nucleus B and the adjacent valence electron μ in the field
of the nucleus A need not be symmetric. Therefore the equations (4.22)
and (4.23) can be rewritten

$$H_{\mu\mu} = U_{\mu\mu} - \sum_{B(\neq A)} V_{AB} \left(\mu \text{ on atom } A \right)$$

(4.25)

$$H_{\mu\nu} = 0 \qquad \left(\mu \neq \nu ; \begin{array}{l} \text{both on the} \\ \text{same atom} \end{array} \right)$$

(4.26)

It is noted that $H_{\mu\nu} \neq 0$ if ϕ_μ and ϕ_ν are on different
atoms which will be discussed in the next approximation.

Approximation E

If ϕ_μ and ϕ_ν are on different atoms, it is only necessary to
consider the possible lowering of energy levels by being in the electro-
static field of two atoms simultaneously which is referred to as a
"Resonance Integral" and is denoted by $\beta_{\mu\nu}$. $H_{\mu\nu}$ can be

approximated as

$$H_{\mu\nu} \cong \beta_{\mu\nu} = \beta_{AB}^{o} \, S_{\mu\nu} \tag{4.27}$$

where β_{AB}^{o} is a parameter depending only on the nature of the atoms A and B. Empirical values will be used for these parameters.

The $F_{\mu\nu}$ matrix elements now reduce to the form from equation (4.19) to (4.27)

$$F_{\mu\mu} = U_{\mu\mu} + \left(P_{AA} - \frac{1}{2} P_{\mu\mu} \right) \gamma_{AA} + \sum_{B(\neq A)} \left(P_{BB}\gamma_{AB} - V_{AB} \right) \tag{4.28}$$

$$F_{\mu\nu} = \beta_{AB}^{o} \, S_{\mu\nu} - \frac{1}{2} P_{\mu\nu} \gamma_{AB} \qquad (\mu \neq \nu) \tag{4.29}$$

where ϕ_{μ} belongs to atom A and ϕ_{ν} belongs to atom B.

Using the same approximations, the total energy is given by one or two atom types from the equation (4.8)

$$E_{total} = \sum_{A} E_{A} + \sum_{A<B} \sum E_{AB}$$

Where

$$E_{A} = \sum_{\mu}^{A} P_{\mu\mu} U_{\mu\mu} + \frac{1}{2} \sum_{\mu}^{A} \sum_{\nu}^{A} \left(P_{\mu\mu} P_{\nu\nu} - \frac{1}{2} P_{\mu\nu}^{2} \right) \gamma_{AA} \tag{4.30}$$

$$E_{AB} = \sum_{\mu}^{A} \sum_{\nu}^{B} \left(2 P_{\mu\nu} \beta_{\mu\nu} - \frac{1}{2} P_{\mu\nu}^{2} \gamma_{AB} \right)$$

$$+ \left(\frac{z_{A} z_{B}}{R_{AB}} + P_{AA} P_{BB} \gamma_{AB} - P_{AA} V_{AB} - P_{BB} V_{BA} \right) \tag{4.31}$$

IV-3. Choice of Parameters of CNDO1 and CNDO2

In the complete neglect of differential overlap approximation, the CNDO1 and CNDO2 methods are different levels of approximation of the equations.

The LCAOSCF Hatree-Fock matrix elements are

$$F_{\mu\mu} = U_{\mu\mu} + \left(P_{AA} - \frac{1}{2}P_{\mu\mu}\right)\gamma_{AA} + \sum_{B(\neq A)}\left(P_{BB}\gamma_{AB} - V_{AB}\right) \quad (4.28)$$

$$F_{\mu\nu} = \beta^{o}_{AB} S_{\mu\nu} - \frac{1}{2}P_{\mu\nu}\gamma_{AB} \quad (\mu \neq \nu) \quad (4.29)$$

where the bonding parameter β^{o}_{AB} is given by

$$\beta^{o}_{AB} = 0.5\left(\beta^{o}_{A} + \beta^{o}_{B}\right) \quad (4.32)$$

In the equation (4.32), β^{o}_{A} is chosen empirically but depends only on the nature of atom A. These values are listed in Table 2. The parameters $U_{2S,2S}$ and $U_{2P,2P}$ can be estimated from ionization potentials, using the theoretical value of γ_{XX} (12).

$$I_{S}(X, 2s^{m}2p^{n}) = E(X^{+}, 2s^{m-1}2p^{n}) - E(X, 2s^{m}2p^{n})$$
$$= -U_{2S,2S} - (m+n-1)\gamma_{XX} \quad (4.33)$$

$$I_{P}(X, 2s^{m}2p^{n}) = E(X^{+}, 2s^{m}2p^{n-1}) - E(X, 2s^{m}2p^{n})$$
$$= -U_{2P,2P} - (m+n-1)\gamma_{XX} \quad (4.34)$$

or

$$-I_{\mu} = U_{\mu\mu} + (Z_{A}-1)\gamma_{AA} \quad (4.35)$$

and the atomic electron affinities A_{μ}'s are used by the formula

$$-A_{\mu} = U_{\mu\mu} + Z_{A}\gamma_{AA} \quad (4.36)$$

Also the equation (4.28) can be rewritten

$$F_{\mu\mu} = U_{\mu\mu} + \left(P_{AA} - \frac{1}{2}P_{\mu\mu}\right)\gamma_{AA}$$

$$+ \sum_{B(\neq A)} \left(P_{BB} - Z_B\right)\gamma_{AB}$$

$$+ \sum_{B(\neq A)} \left(Z_B \gamma_{AB} - V_{AB}\right) \qquad (4.28)'$$

where the last term of equation (4.28)' is described as penetration

integral contributions to $F_{\mu\mu}$.

The following table gives the approximate form between CNDO1 and

CNDO2.

TABLE 4

Difference between CNDO1 and CNDO2

reference	CNDO1	CNDO2
$-U_{\mu\mu}$	$I_\mu + (Z_A - 1)\gamma_{AA}$	$\frac{1}{2}(I_\mu + A_\mu) + (Z_A - \frac{1}{2})\gamma_{AA}$ (4.37)
$F_{\mu\mu}$	$U_{\mu\mu} + (P_{AA} - \frac{1}{2}P_{\mu\mu})\gamma_{AA}$ $+ \sum_{B(\neq A)}(P_{BB}\gamma_{AB} - V_{AB})$	$U_{\mu\mu} + (P_{AA} - \frac{1}{2}P_{\mu\mu})\gamma_{AA}$ $+ \sum_{B(\neq A)}(P_{BB} - Z_B)\gamma_{AB}$ (4.38)

Where 1 the average ionization potentials I_μ (e.v.) used to fix $U_{\mu\mu}$ are listed in Table 3.
2 the matrix elements $\frac{1}{2}(I_s + A_s)$ and $\frac{1}{2}(I_p + A_p)$ are listed in Table 5.

TABLE 5

Matrix Elements From Atomic Data (e.v.)

	H	Li	Be	B	C	N	O	F
$\frac{1}{2}(I_a + A_a)$	7.176	3.106	5.946	9.594	14.051	19.316	25.390	32.272
$\frac{1}{2}(I_p + A_p)$		1.258	2.563	4.001	5.572	7.275	9.111	11.080

If the penetration integral term in equation (4.28)' was neglected
to avoid the excess bonding and high value of force constants, then
equation (4.28)' can be reduced to the form of (4.38). This corresponds
to substituting the following term for CNDO2 from CNDO1:

$$V_{AB} = Z_B \gamma_{AB} \qquad (4.39)$$

Using parameters specified in the above way, the LCAOSCF equations are
solved in the following steps:

(a) An initial set of M.O. coefficients $C_{\lambda\mu}$ is obtained from
a "Hückel type" calculation such that $F_{\mu\mu}$ is replaced by
average ionization potential and $F_{\mu\nu}$ by $\beta^\circ S_{\mu\nu}$.

(b) Electrons are assigned in pairs to the M.O.'s with lowest energies.

(c) Calculated $P_{\mu\mu}$ and $P_{\mu\nu}$ are used to form a new Hatree Fock
matrix element $F_{\mu\nu}$.

(d) New coefficients $C_{\lambda\mu}'s$ are derived from this $F_{\mu\nu}$ and the
process is repeated from step (b) until self-consistency is
achieved on all coefficients with a tolerance of 0.0001.

V. Discussion of Results

The molecules selected for these calculations are as follows:
Hydrogen molecule (H_2), Lithium molecule (Li_2), Beryllium (Be_2),
Nitrogen molecule (N_2), Fluorine molecule (F_2), water molecule (H_2O),
Ammonia molecule (NH_3), Ethane molecule (C_2H_6), oxygen difluoride
(F_2O), Difluorodiazine (N_2F_2), Methane (CH_4), Methylfluoride (CH_3F)
and Hydrogen Peroxide (H_2O_2). These calculations will show the minimum
configurations for bond lengths, bond angles, force constants, the

energy level considerations for NH_3 and F_2O, and the Barrier for NH_3, C_2H_6, N_2F_2 and H_2O_2. Finally the calculations will extend the variation of parameters to fit the experimental potential surfaces.

V-1. Comparison of the equilibrium configurations and force constants

The ASCFT calculations with various inter-nuclear distances and bond angles are useful in predicting equilibrium bond lengths and bond angles. These results are listed in Table 6. The equilibrium configurations (bond lengths and bond angles) are in fairly good agreement with experimental values but the force constants are too high compared with the experimental values by a factor of about 2.0. This can be improved by adjusting parameters, such as the Slater exponent and β°. Sample results are discussed in Section V-9.

TABLE 6						
Comparison of Bond Lengths, Bond Angles & Force Constants (k_r & k_θ)						
	Bond Length (A°)(13)		Bond Angle (deg)(13)		Force Consts	$\begin{pmatrix} k_r: 10^5 \ dyne/cm \\ k_\theta: 10^{-11} \ erg/rad^2 \end{pmatrix}$
	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.
H_2	0.7459	0.7415			10.143	5.6
N_2	1.1395	1.0976			52.160	23.10 (14)
H_2O	1.0289	0.958	104.22	104.45	17.260 / 0.845	8.23 / 0.694 (14)
NH_3	1.0657	1.015			14.68	6.86
			106.825	106.6	0.95	0.60 (14)
CH_4	1.1135	1.1135			12.65	5.45
			109.47	109.47		0.498 (15)
C_2H_6 D_3d R_{CH}	1.1195	1.102			12.12	5.35
R_{CC}	1.4633	1.543			16.34	4.57
$\angle HCH$			107.76	109°37'		0.51 (16)
$\angle CCH$			110.86	109°37'		0.63

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V-2. Water molecules (H_2O)

For H_2O, C_{2v} symmetry was assumed with an O-H bond length of 0.96A°. The first calculation shows an energy minimum at a bond angle of 107.28°. At this bond angle, the equilibrium O-H bond length of 1.0289A° is obtained. With this bond length, the second calculation shows the bond angle of 104.22° at which the O-H bond length is calculated to be 1.0289A°. This is in satisfactory agreement with the experimental bond angle of 104.45° (13). These calculations demonstrate the O-H bond stretching and angle HOH bending motion such that the O-H bond lengths tend to have symmetrical stretching motion and the bond angle tends to have scissoring motion (symmetrical in-plane deformation). A series of these calculations is listed in Table 7. The stretching force constant is calculated to be 17.26×10^5 ($dyne/cm$) which is higher by a factor of 2.1 with respect to the experimental value of 8.23×10^5 ($dyne/cm$). The bending force constant is calculated to be 0.845×10^{-11} (erg/rad^2) which is higher by a factor of 1.22 than the experimental value of 0.694×10^{-11} (erg/rad^2) (14).

TABLE 7			
Calculation of R_{OH} and $\angle HOH$ for H_2O			
	Calculation I	Calculation II	Experiment
R_{OH}(A°)	0.96 (Exp)	1.0280	0.958
$\angle HOH$	107.28	104.22	104.45
* The computer outputs (sample) are listed in Appendix 2.			

V-3. Ammonia Molecule (NH_3)

The ammonia molecule with an NH bond length of 1.05A° (13) is calculated to be non-planar with an $\angle$ HNH bond angle of 106.825°

which is in close agreement with the experimental value of 106.6° (13). At this value of the bond angle, the NH bond length was found to be 1.0657 A°. The subsequent calculation shows a bond angle of 104.86° and again the bond length of 1.0673 A°. On the other hand the equilibrium bond length for the planar configuration gives 1.0543 A°. It is interesting when calculations presented here are compared with results recently calculated by R. Moccia and L. Randaccio (17). They reported the minimum bond length of 1.878 a.u. (0.9938A°) at a bond angle of 105°36' and a bond length of 1.837 a.u. (0.9721 A°) at a planar configuration. The change in minimum bond length between non-planar and planar configuration is 0.0217 A° by Moccia and 0.0114 A° by the ASCFT. The smaller value of this bond length change in the present calculation is due to the higher stretching force constants for ASCFT. Also, subsequent calculations can predict the symmetrical bond stretching motion and symmetrical in-plane deformation of bond angle for the ground state of this molecule. The stretching force constants are calculated to be 14.64×10^5 (dyne/cm). This differs by a factor of 2.14 with respect to the experimental value of 6.86×10^5 dyne/cm (14) and the bending force constants are calculated to be 0.95×10^{-11} erg/rad.^{2} (factor of 1.58 with respect to experimental values of 0.6×10^{-11} erg/rad^2 (14)).

It is also interesting to compare the barriers calculated by the several methods and the difference in barriers with respect to adjusting the various parameters. These are listed in Tables 8 and 9, respectively.

TABLE 8

Comparison of the results of Calculations for NH3

Reference	Method of calculations	R_{NH} (a.u)	$\angle HNH$ (deg)	Pyramid Height(a.u.)	Barrier Height(a.u.)
Present Calc.	Approximate (CNDO) SCF MO	1.9923	106°49'	0.749	0.0251
Higuchi (18)	Approximate polycenter SCF MO	1.916	108.0	0.592	0.0147
Kaplan (19)	Single Determinant polycenter SCF MO	1.916	106°47'	0.719	0.146
Moccia (20)	Single Determinant one center SCF MO	1.928	110°2'	0.6245	0.0027
Joshi (21)	Single determinant one center SCF MO	1.867	109°34'	0.626	0.0411
Moccia (17)		1.878	105°36'	0.739	0.00905
Experiment		1.9162	106°47'	0.719	0.0092 (22)

From Table 9, it is interesting to compare the change in barrier
with respect to a change in bond angles at the fixed bond length of
1.0657A° (Calculation II and IV) such that the change in barrier is
0.000030279 a.u. (0.002540830 - 0.002510551) and the change in bond
angle is 1.965° (106.825° - 104.86°). From this calculation, it is
found that the calculated barrier is 0.002540830 a.u. which is different
by only 1.2% from the first calculated barrier.

The electronic configuration is found to be

$$(1a_1)^2 \ (1e)^4 \ (2a_1)^2 \ a_1 \ .$$

Configurations calculated by ASCFT, EHT and full LCAOSCFT by H. D.
Joshi (21) are compared in Fig. 1 and Fig 2. There is complete agreement
between ASCFT and full LCAOSCFT calculations for the orbital energies
as a function of height of pyramid. It is noted that the lowest orbital

FIG. 1. E_{tot}. AND ℰ_{orb}. OF NH₃ AS FUNCTION OF PYRAMID HEIGHT.
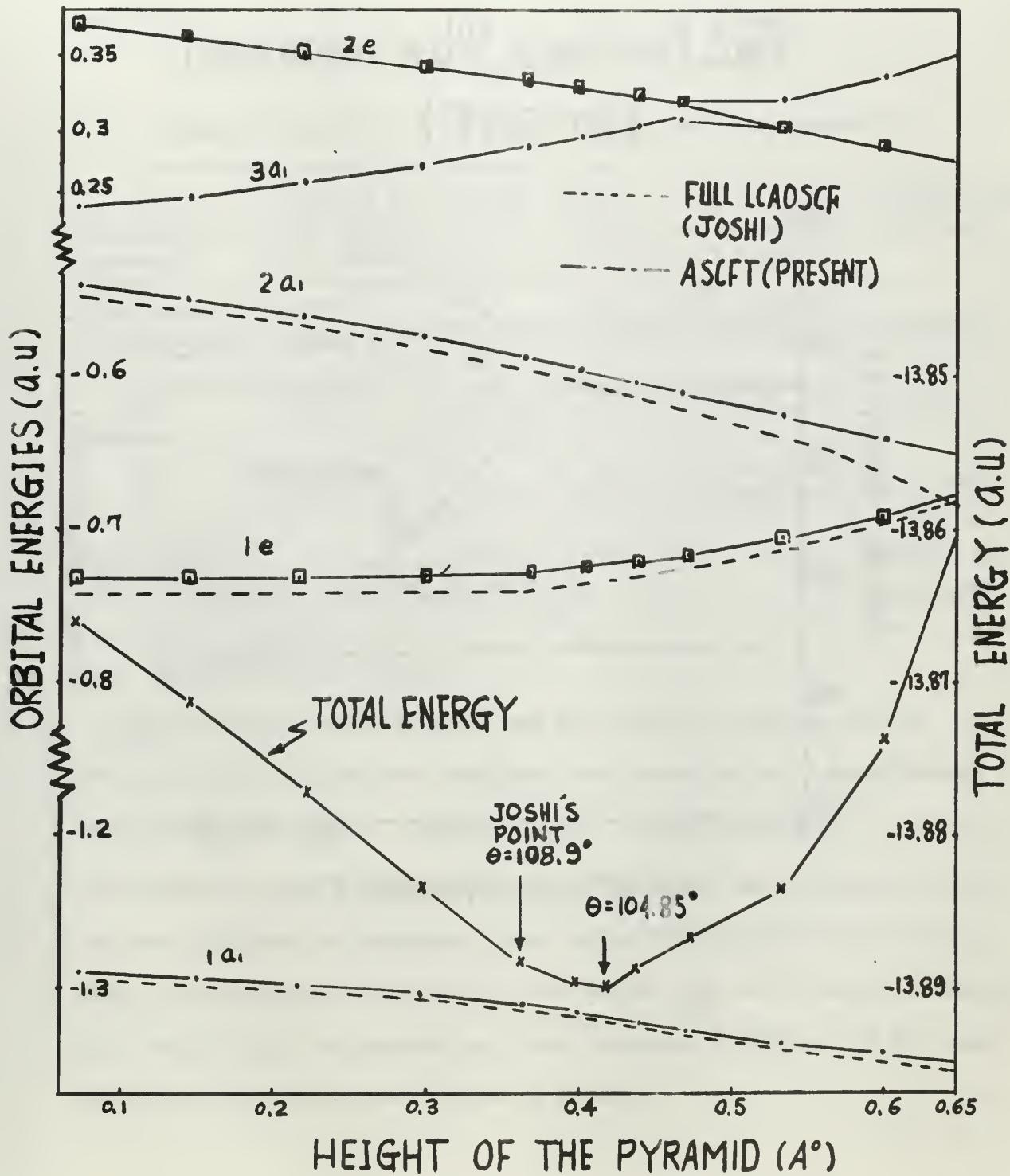
Fig. 2. E_tot. & E_orb. of NH₃ vs. Pyramid Height (By EHT)

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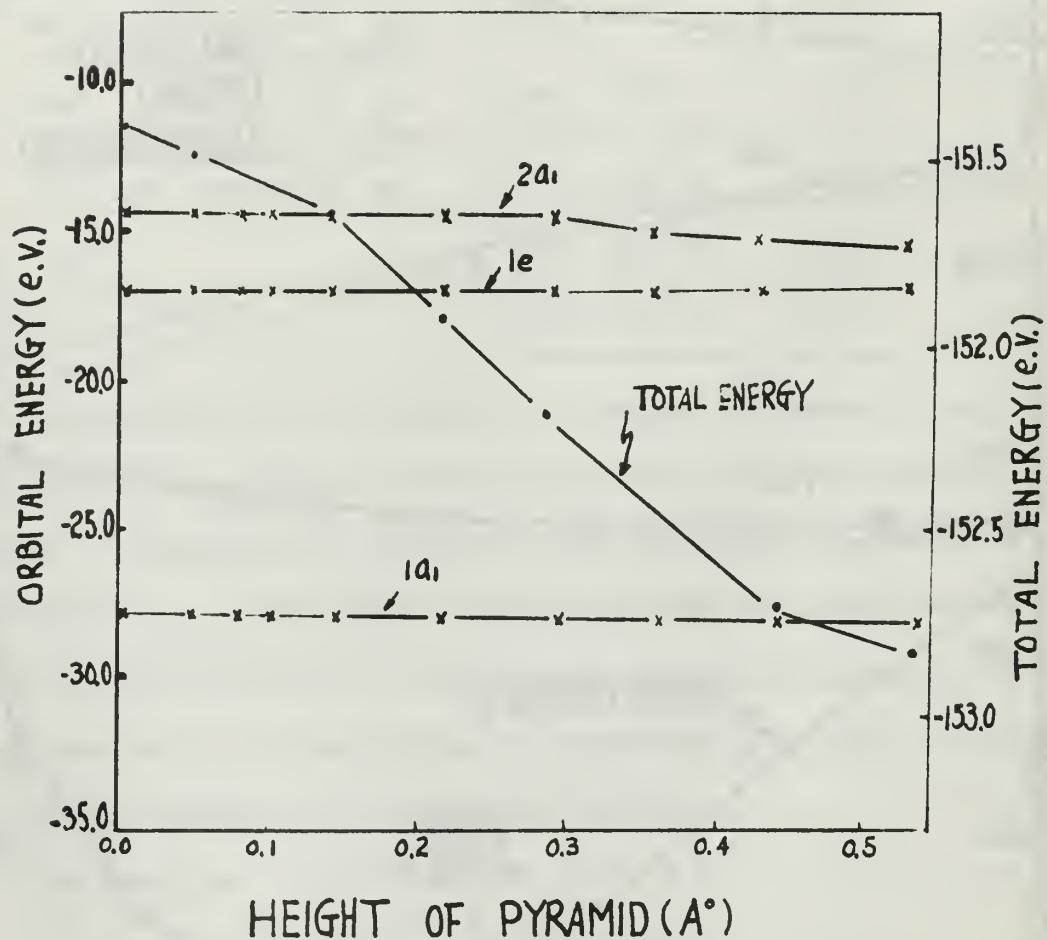
energy in LCAOSCFT calculation is due to the (1s) electron (inner-shell) of Nitrogen but ASCFT neglects that part. On the other hand, the EHT calculation (Fig. 2) does not even demonstrate a double minimum potential curve. Therefore the EHT is quite inferior for this kind of molecule.

TABLE 9

Change in Barrier for NH3 w.r.t. minimizing the parameter

	$R_{\overline{NH}}$ $(A°)$	$\angle \overline{Z}NH$	$\angle HNH$	E_{total} $(a.u.)$	Barrier (a.u.)
Calculation I (General)	1.02 (fixed) 1.02 (fixed)	o 112.0	120 106.825	-13.85761125 -13.87775028	0.02013903
Calculation II (Equilibrium)	1.0543 1.0657	o 112.0	120 106.825	-13.86430636 -13.88941245	0.02510551
III	1.0543 1.0543	o 113.18	120 105.10	-13.86430636 -13.88890154	0.02453518
IV	1.0657 1.0657	o 113.55	120 104.86	-13.86362706 -13.88971466	0.02608760
Experimental		112.206	106.6		0.0092
* The true Barrier for this calculation is (13.88971466 – 13.86430636) (a.u.)					0.02540830

V-4. Ethane molecule (C_2H_6)

Calculations based on ASCFT and EHT have been carried out for Ethane in both eclipsed and staggered configurations with experimental values such that $R_{\overline{CC}}$ = 1.543A°, $R_{\overline{CH}}$ = 1.102A° and $\angle CCH$ = 109°37' (tetrahedral angle). The first calculation shows the equilibrium angle for both eclipsed and staggered forms using EHT and ASCFT. The energy then was minimized by varying the bond length $R_{\overline{CC}}$, and finally by varying bond length $R_{\overline{CH}}$. The stretching force constants ($k_{\overline{CC}}$ and $k_{\overline{CH}}$) were found and those values are listed in Table 10.

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It is of interest to look at the barrier resulting in the change in geometry. These changes in parameters and the corresponding barriers are compared in Table 11. These comparisons show that the eclipsed form is more open than the staggered form by a few tenths of a degree; also the bond length $R_{\overline{CC}}$ is elongated a few thousandths of an Ångstrom and the bond length $R_{\overline{CH}}$ is shortened a few ten thousandths of an Ångstrom. Some researchers have shown an elongation for $R_{\overline{CH}}$. Although these changes ($R_{\overline{CH}}$) in geometry are small, their effect on the internal-rotation barrier is very significant.

TABLE 10

Comparison of Ethane Betn. EHT & ASCFT Calculation

Reference	Calculated				Expt. (16)
	ASCFT		EHT		
	Eclipsed	Stagger	Eclipsed	Stagger	D3d
$\angle CCH$	111.28	110.86	110.99	110.44	109°37'
$\angle HCH$	107.60	108.04	107.90	108.48	109°37'
$R_{\overline{CC}}$	1.4660	1.4633	1.8070	1.8000	1.543
$R_{\overline{CH}}$	1.1193	1.1195	0.9086	0.9088	1.102
$k_{\angle CCH} \left[10^{-11} \frac{erg}{rad.^2} \right]$	(1.74)	(1.67)	(8.85)	(8.8)	0.63
$k_{\angle HCH}$	( )	( )	( )	( )	0.51
$k_{\overline{CC}} \left[10^5 \frac{dyne}{cm} \right]$	15.887	16.340	197.0	184.0	4.57
$k_{\overline{CH}}$	12.125	12.124	164.05	186.56	5.35
Barrier ($\frac{kcal}{mole}$)	2.3288		2.6586		$2.875^{+}_{-}.125$ -(23)

There is some uncertainty in the Table 11 for EHT calculation. Every reported calculation scheme has the same tendency to increase the barrier when the parameters are changed in sequence, but EHT

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calculation shows the barrier is decreased. The resultant barrier by EHT is 1.6358 ^{kcal}/mole. This is not in agreement with the value 2.6586 ^{kcal}/mole found by varying only one parameter, $\angle CCH$, holding the other two parameters $R_{\overline{CC}}$ and $R_{\overline{CH}}$ constant. It is noted that R. Hoffmann (1) reported 4.0 ^{kcal}/mole with a Slater exponent (H) of 1.0. Present calculations use the value of 1.2. However the results are in fairly good agreement with experimental values using both ASCFT and EHT (with some uncertainty).

TABLE 11						
Comparison of Barrier for Ethane						
Reference	$\triangle$ Parameter(Ecl.—Stag)			Barrier(Eclip.—Stag)		
	$\angle CCH$ (deg)	R_{CC} (A')	R_{CH} (A°)	$\angle CCH$	R_{CC}	R_{CH}
T.L.Hill[24] (1948)	0.34	0.0054	0.0002	0.613	0.665	0.700
L.S. Bartell[25] (1960)	0.20	0.0029	0.0001	0.367	0.383	0.394
J.T.Vanderslice[26] & E.A.Mason(1960)	0.17	0.0024	-0.0001	0.387	0.416	0.434
L.Salem[27] (1962)	0.05	0.0007	0.0000	0.104	0.106	0.107
K.E.Howlett[28] (1960)	0.40	0.0059	-0.0002	0.779	1.108	1.298
V.Magnasco[29] (1962)	0.55	0.0080	-0.0011	-1.532	1.675	2.944
O.J.Sovers & [30] M.Karplus (1966)	0.20	0.0029		2.311	3.611	
Present (ASCFT)	0.42	0.0027	-0.0002	1.8637	2.2848	2.3288
(EHT)	0.55	0.0070	-0.0002	2.6586	1.5746	1.6358
Expt.	3.03±0.3(^{kcal}/mole) (31)			2.875±0.125 (^{kcal}/mole) (23)		

V-5. Methane (CH_4) and Methylfluoride (CH_3F)

Calculations between methane and methylfluoride were carried out using tetrahedral symmetry for methane and C3v symmetry for methylfluoride with $R_{\overline{CH}} = 1.1135A^\circ$ for CH_4 and $R_{\overline{CH}} = 1.109$ and $R_{\overline{cF}} = 1.385$ for CH_3F. The calculated values for the equilibrium configurations are listed in Table 12. The force constants are calculated for each molecule and these are listed in Table 12. The stretching force constants are different by a factor of 2.3 for CH_4 and 2.5 for CH_3F with respect to their observed values (15).

For a methane molecule, the calculated bond lengths and bond angles are the same as the observed values.

For methylfluoride molecules, the bond angle $\angle$ HCH is more open than the angle of $\angle$ HCF which can be explained as follows: there exists rehybridization for the CH_3F molecule because there must be more P-character in C-F bond due to the electron withdrawing fluorine; on the other hand, there must be more S-character in C-H bond which gives more SP^2 hybrid character for the C-H sigma (σ) bonds. It is obvious that the SP^2 hybrid orbital is more planar than SP^3. Therefore $\angle$ HCH is more open. It is here that the best agreement between theoretical and calculated results was found.

TABLE 12

Comparison of Γ , Θ and kr & kθ between CH_4 & CH_3F

	Bond Length (A°)		Bond Angle (deg)		Force Consts.	
	Cal.	Obs.	Cal.	Obs.	Cal.	Obs.
CH_4	1.1135	1.1135			12.65	5.45
			109.47	109.47	(.745)	0.498
R_{CH}	1.1180	1.109			12.09	4.71(15)
R_{CF}	1.3458	1.385			23.57	5.64(15)
CH_3F $\angle HCH$			110.382	109.997		0.443(15)
$\angle FCH$			108.54	108.94	(1.77)	0.792(15)

V-6. Difluorodiazine (N_2F_2)

Calculations have been carried out for difluorodiazine in both trans and Cis configurations with R_{NN} = 1.25A°, R_{NF} = 1.44A° and $\angle NNF$ = 115° (13). In both configurations, the new equilibrium distances and bond angles are determined and are listed in Table 14. When comparisons are made of the equilibrium geometry in Table 14, the bond angle $\angle NNF$ is more open for Cis than trans configurations. Significantly, the bond length R_{NN} is elongated a few thousanths more for trans than Cis (same for R_{NF}).

It is of interest to compare the energy level difference between Cis and trans configurations. The experimental results giving the stability between both configurations are listed in Table 13. In 1963, Armstrong and Marantz published that the Cis form is more stable by 3.0 ± 0.3 ^{kcal}/mole (36) (refer also (37)). The present calculation predicts the Cis form to be more stable by 3.249 ^{kcal}/mole than the trans (C_2h) form. Fortunately, these results are in most satisfactory

agreement with experimental value. In Table 14 are compared the differences in energies between the Cis and trans configurations for a variation in molecular parameters. First the angle $\angle NNF$ was varied to minimize the energy. With this bond angle, the minimum bond length R_{NN} was calculated and finally the minimum bond length R_{NF} was found. In each case, the difference in energies was compared with the one obtained initially. It was found that there is no effect due to varying the angle $\angle NNF$ and bond length R_{NN} but there is a very significant difference when the bond length R_{NF} was minimized. This result shows the configuration is affected significantly due to the R_{NF} stretching motion.

TABLE 13			
Results of experiments for N_2F_2 (stability)			
Year Author		Reference	Results
1947 S.H. Bauer [32]		J.Am.Chem.Soc.,69,3104	trans is more stable than Cis configuration
1959 C.B. Colburn,et.al. [35]		" " " " ,81,205	
1960 R.H. Sanborn [34]		J.Chem.Phys., 33,1855	Cis and N=N<^F_F is more chemically active isomer
1961 R. Ettinger,et.al. [35]		" " " , 34,2187	
1963 G.T. Armstrong [36] & S. Marantz		J.Chem.Phys., 38,169	Cis is more stable by 3.0 ± 0.3 kcal/mole
Present			Cis is more stable by 3.249 kcal/mole

The next interesting calculation is the barrier due to the rotational motion which was reported by the Binenboyn (37) . It was reported by experiment to be 32.0 kcal/mole and calculated to be 84 kcal/mole (36) between trans and linear configuration. However, the present calculations were carried out in various ways and those results are listed in Table 15. The calculated barrier between linear and trans form in

Calculation	Parameters			Δ Par(C_{2v} - C_{2h})			Diff. in Barrier
	$\angle NNF$ (deg)	R_{NN} (A°)	R_{NF} (A°)	$\angle NNF$	R_{NN}	R_{NF}	ΔE (C_{2v} - C_{2h})
I General	115 115	1.25 1.25	1.44 1.44	0	0	0	0.2553 (0)
II C_{2v} C_{2h}	109.98 104.09	1.25 1.25	1.44 1.25	5.89	0	0	0.2553 (0)
III C_{2v} C_{2h}	109.98 104.09	1.2197 1.2218	1.25 1.25	5.89	-0.0021	0	(-)0.04962 (.31)
IV C_{2v} C_{2h}	109.98 104.09	1.2197 1.2218	1.2410 1.2441	5.89	-0.0021	-0.0031	(-)3.2492 (3.5)
Expt. value							(-)3.0±0.3

TABLE 14

Equilibrium Configuration Btn. C_{2v} & C_{2h} for N_2F_2

Table 15 is too high with respect to the reported barrier but the calculation between trans and C2 form shows a satisfactory agreement with the calculated (38) and experimental value (39). It must be noted that when an attempt was made to calculate the rotational barrier, no dihedral angle exists; that is, when the dihedral angle is 90 degrees, the bond angle $\angle NNF$ turns out linear, and also the dihedral angle does not exist and the motion is predicted to be an up and down motion which is shown in Calculation IV and V in Table 15. The calculated barriers are illustrated in Fig. 3.

TABLE 15

Comparison of Barrier for N_2F_2

No.	Ref.	Parameters			Etot. (a.u.)
		∠NNF	R$\overline{nn}$	R$\overline{nf}$	
I	C2v (Cis)	109.98	1.2197	1.2410	-78.87407234
II	C2h (trans)	104.09	1.2218	1.2441	-78.86889607
III	0.5(I + II)	107.035	1.22075	1.24255	-78.87148421
IV	C2(__.__)	114.07	1.2208	1.2426	-78.75824577
V	C$_2$vo (—·—·—)	180.0	1.2119	1.440$_*$	-78.54333813
Barrier	E(II) - E(IV) = 69.456	E(II) - E(IV) = 204.356	E(I) - E(IV) = 72.7057	E(I) - E(V) = 207.657 kcal/mole	
Exp.	E(II) -- E(V) = 32 kcal/mole (37)				
Cal.	E(II) -- E(V) = 84 kcal/mole (36)				

Fig. 3 Barrier for N_2F_2 as function of XNF
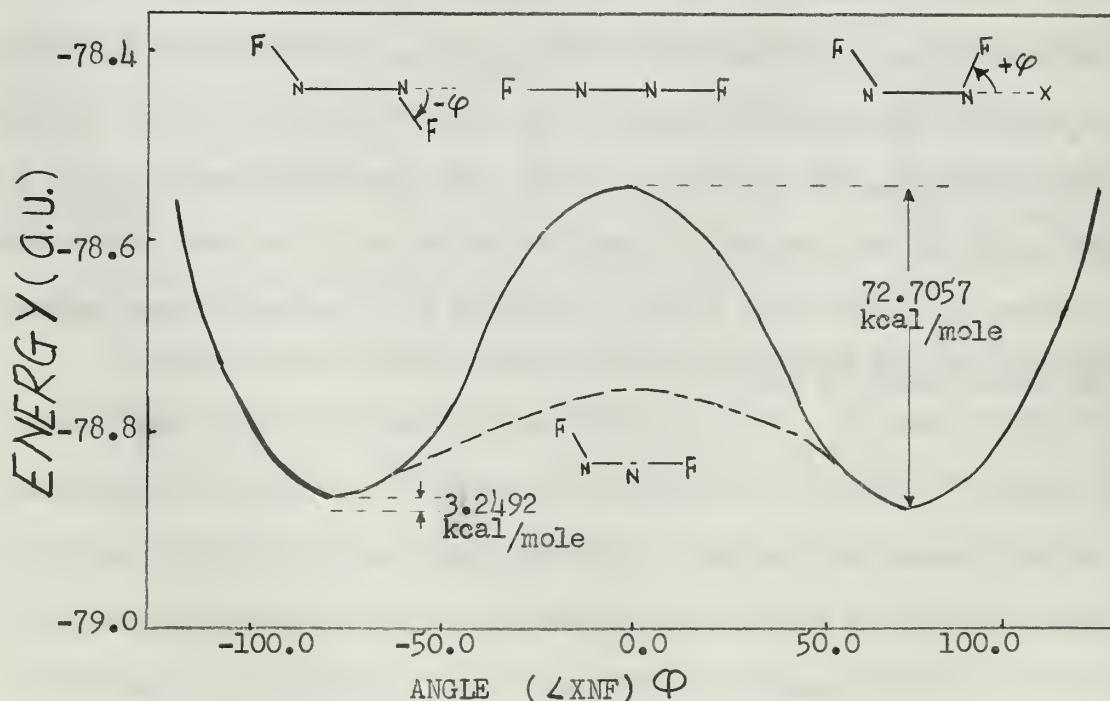
V-7. Oxygen difluoride (F_2O)

For the F_2O molecule with C_2v symmetry ($R_{\overline{OF}} = 1.41A^\circ$ (13)), the lowest energy configuration is calculated to be bent with an $\angle FOF = 97.16^\circ$ (at fixed $R_{\overline{OF}} = 1.50A^\circ$) as compared with the experimental angle of 103.8° (38). The bond length $R_{\overline{OF}}$ (at angle of 97.16°) is calculated to be $1.1792A^\circ$. Also the bending and stretching force constants are calculated to be 1.1497×10^{-11} erg/rad^2 (observed $k_{\angle FOF} = 0.55 \times 10^{-11}$ erg/rad^2) and 40.94×10^5 dyne/cm (observed $k_{\overline{OF}} = 5.57 \times 10^5$ dyne/cm (14)).

It is of interest to compare the orbital energies as a function of internuclear angle with that publisted by Buenker and Peyerimhoff (39). The calculated results are illustrated in Fig. 4 and these were compared with c alculations by Buenker and Peyerimhoff (using full LCAOSCF theory) also in Fig. 4. The comparison in Fig. 4 shows a satisfactory agreement except for $5a_1$, $1b_1$ and $3b_2$. It is noted that, in full LCAOSCF calculation, the lowest doubly degenerate orbitals (due to 1s electrons of two Fluorines) and the next singly degenerate orbital (due to the 1s electron of Oxygen) were neglected. Therefore the comparison is valid starting with the third level in the Fig given by Buenker.

FIG. 4. ORBITAL ENERGY OF F_2O AS FUNCTION OF ∠FOF.
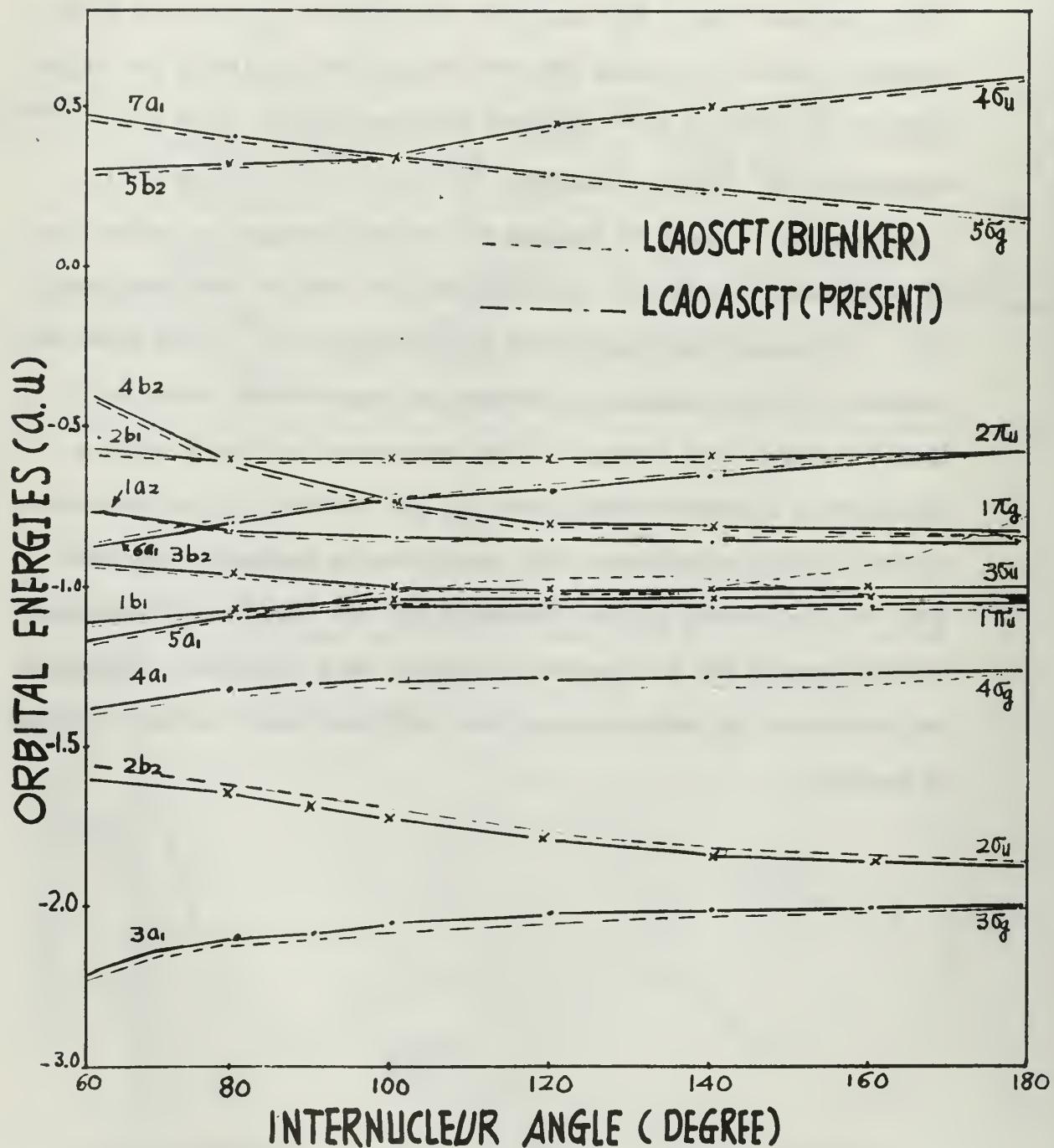
V-8. Hydrogen Peroxide (H_2O_2)

For the hydrogen peroxide molecule, the calculations were performed to find the barrier and the equilibrium configurations with $R_{\overline{OH}}=0.97A^O$, $\angle HOO=100^O$, $R_{\overline{OO}}=1.49A^O$ and dihedral angle of 93.6^O (13). Unfortunately, the present calculation does not show the existence of a dihedral angle. The result of the calculation shows that there exists a Cis and trans configuration for H_2O_2 just as for N_2F_2. The structural parameters are illustrated in Fig. 5.

Fig. 5 Structural Parameters $\left(H_2O_2 \right)$
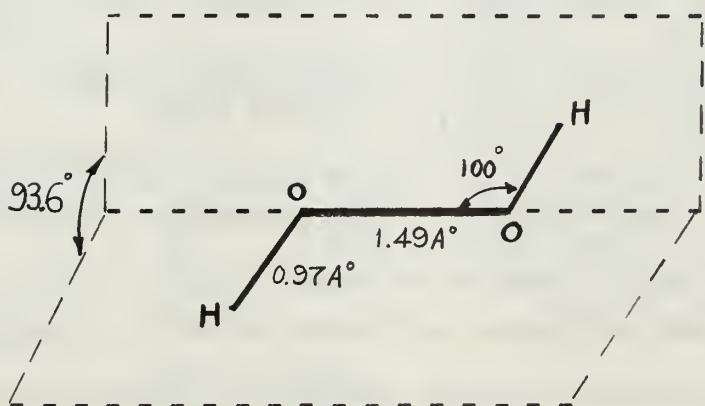
V-9. Homonuclear diatomic molecules

For the diatomic molecules, the equilibrium configurations of H2, Li2, N2 and F2 were calculated. An attempt was made to find a new set of optimized parameters by changing the Slater exponents and beta zeroes (β°). The equilibrium bond lengths and force constants are listed in Table 16. It is noted that B2, C2 and O2 molecules are excluded in the calculations because they are ground state triplets, and the Be2 molecule is non-bonded. The necessary partial derivatives were found and listed in Table 16.

TABLE 16
Equilibrium Configurations and Some Partial derivatives for homo nuclear diatomic molecules

	Re (A$^\circ$)		$k_r (10^5 \, dyne/cm)$		average partial between (S.E)$_0 \pm$ 0.1 and also $\beta^\circ \pm$ 1.0			
	Cal.	Obs.	Cal.	Obs.	$(\partial R/\partial s)_{\beta^\circ}$	$(\partial R/\partial \beta^\circ)_s$	$(\partial k_r/\partial s)_{\beta^\circ}$	$(\partial k_r/\partial \beta^\circ)_s$
H2	0.746 (0.89)	0.74	10.14 (6.5)	5.6	−0.54	−0.34	19.18	1.0555
Li2	2.179 (2.788)	2.67	0.84 (0.41)	0.25	−2.94	−0.022	3.07	0.52
N2	1.14	1.09	52.16	23.10	−0.47	−0.01	61.06	2.34
F2	1.12	1.44	56.41	4.45				

For those molecules, an attempt was made to find a new set of optimized parameters fitting experimental equilibrium bond lengths and force constants. The Slater exponent and β° were considered in adjusting the parameters to optimize agreement for calculated potential surfaces. The procedures used to find a new set of Slater exponents and beta zero (β°) were as follows:

First: Change the Slater exponent by $\pm$ 0.1 and beta zero by $\pm$1.0, then find the calculated equilibrium bond length and force constant.

Second: Find the partial derivatives
$$\left(\frac{\partial R}{\partial S}\right)_{\beta^\circ}, \quad \left(\frac{\partial k_r}{\partial S}\right)_{\beta^\circ}, \quad \left(\frac{\partial R}{\partial \beta^\circ}\right)_S \quad and \quad \left(\frac{\partial k_r}{\partial \beta^\circ}\right)_S$$
where "S", stands for Slater exponent.

Third: Find the new Slater exponent and   by following equations:
$$dR = \left(\frac{\partial R}{\partial S}\right)_{\beta^\circ} dS + \left(\frac{\partial R}{\partial \beta^\circ}\right)_S d\beta^\circ \tag{5.1}$$

$$dk_r = \left(\frac{\partial k}{\partial S}\right)_{\beta^\circ} dS + \left(\frac{\partial k}{\partial \beta^\circ}\right)_S d\beta^\circ \tag{5.2}$$

then approximate the dR, ds and   as follows:

$$dR \cong \Delta R = R_{equ.} - R_{cal.}$$

$$dS \cong \Delta S = S_{new} - S_{cal.}$$

$$d\beta^\circ \cong \Delta\beta^\circ = \beta^\circ_{new} - \beta^\circ_{cal.} \tag{5.3}$$

Fourth: Solve equation (5.1) and (5.2) to find the new Slater exponent
and β° . For example:

(1) H_2 molecule:
$$\begin{bmatrix} -0.06 \\ -4.83 \end{bmatrix} = \begin{bmatrix} -5.4 & -3.4 \\ 19.18 & 1.055 \end{bmatrix} \longrightarrow \begin{bmatrix} -0.277 \\ 0.457 \end{bmatrix} = \begin{bmatrix} \Delta S \\ \Delta\beta^\circ \end{bmatrix}$$
therefore
$$S_{new} = 0.923$$
$$\beta^\circ_{new} = 9.457 \tag{5.4}$$

(2) Li_2 case:
$$\begin{bmatrix} -0.49 \\ -0.59 \end{bmatrix} = \begin{bmatrix} 2.94 & 0.022 \\ 3.07 & 0.52 \end{bmatrix} \longrightarrow \begin{bmatrix} -0.164 \\ -0.410 \end{bmatrix} = \begin{bmatrix} \Delta S \\ \Delta\beta^\circ \end{bmatrix}$$
therefore
$$S_{new} = 0.49$$
$$\beta^\circ_{new} = 8.59 \tag{5.5}$$

(3) N_2 case:
$$\begin{bmatrix} -0.05 \\ -29.06 \end{bmatrix} = \begin{bmatrix} -0.47 & -0.01 \\ 61.06 & 2.34 \end{bmatrix} \longrightarrow \begin{bmatrix} 0.87 \\ -35.5 \end{bmatrix} = \begin{bmatrix} \Delta S \\ \Delta\beta^\circ \end{bmatrix}$$
therefore
$$S_{new} = 2.87$$
$$\beta^\circ_{new} = -9.5 \tag{5.6}$$

From these results, (5.4)and (5.5) are consistent but (5.6)
is completely inconsistent because the force constant is too
high.

Fifth: Finally, repeat the calculation using the above new set of
input parameters (Snew and β° new). The result for the H_2
and Li_2 molecules are listed in parentheses in Table 16.

VI. CONCLUSION

The Approximate Self-Consistent Field M.O. theory was applied
to the calculation of electronic structure for several selected mole-
cules and these results were compared with results by full LCAOSCFT
calculations, if they were available. The most important features of
these calculations are to predict equilibrium configurations (bond
length and bond angle) and the barrier by the variation of internuclear
distances and angles using the ASCFT. The EHT calculations are limited
tc hydrocarbons which give good results (refer to calculation of Ethane
molecule). In general, the barrier predicted by ASCFT calculation is
in satisfactory agreement with the experimental value.

An attempt was made to find a new set of input parameters (Slater
exponent and β°) to improve the prediction of potential surfaces
for certain homonuclear diatomic molecules but the attempt failed
except for the H_2 and Li_2 molecules (see Table 16).

The features of Potential Surfaces of molecules can be predicted
with the approximate self-consistent field theory. Qualitatively, the
agreement between calculations and experimental observations is quite
good. It is conceivable that, with the adjustment of certain parameters

such as resonance integrals (β^o), Slater exponents and penetration integrals, quantitative agreement with experimental results can be obtained.

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APPENDIX

I   Computer program for Approximate Self-Consistent Field
Theory (ASCFT)

```
-COOP.,  YOu      BOX 41  .5/15/25.20.0000.
-FTN.E.L.P.
      PROGRAM DUMMY
      DIMENSION IPT(5), Z(18), ZS(18), BETA(40), U(40), COORD(3,18),
     1F(4 ,40), S(40,40), C(40,40), P(40,40), COS(3,18,18), PA(18),
     2V(18,18), G(18,18), E(18,18), RAD(18,18), RHO(18,18), TAU(18,18),
     3ISTP(18), AL(18), TH(18), PH(18), BONDL(18), AW(18),
     4PP(40,40), PB(18)
C  THIS IS A DUMMY PROGRAM WHICH FIRST CALLS FOR INPUT DATA AND
C  THEN PERFORMS THE CNDO OPERATIONS
    1 CALL INPUT(N,NH,NO,IPT,ISTP,AL,TH,PH,BONDL,Z,ZS,BETA,U,COORD,AW)
      CALL CNDO (N,NH,NO,L,T,,Z,ZS,BETA,U,COORD,F,S,C,P,COS,PA,V,G,E,ET,
     1RAD,RHO,TAU,PP,PB)
      GO TO 1
      END
      SUBROUTINE CNDO (N,NH,NO,IPT,Z,ZS,BETA,U,COORD,F,S,C,P,COS,PA,V,
     1G,E,ET,RAD,RHO,TAU,PP,PB)
      DIMENSION IPT(5), Z(18), ZS(18), BETA(40), U(40), COORD(3,18),
     1F(4 ,40), S(40,40), C(40,40), P(40,40), COS(3,18,18), PA(18),
     2V(18,18), G(18,18), E(18,18), RAD(18,18), RHO(18,18), TAU(18,18),
     3PP(40,40), PB(18)
C  N IS THE NUMBER OF ATOMS IN THE MOLECULE
C  NH IS THE NUMBER OF HYDROGEN ATOMS IN THE MOLECULE
C  NO IS THE NUMBER OF ORBITALS WHICH OCCUPY ELECTRONS
C  IPT(1) = 1 IF COORDINATES, DIRECTION COSINES, THE DISTANCE MATRIX,
C      THE RHO MATRIX, THE TAU MATRIX, THE OVERLAP MATRIX, THE F MATRIX,
C      THE GAMMA MATRIX, AND THE V MATRIX IS TO BE PRINTED OUT.  IF NO
C      PRINT OUT OF THESE IS DESIRED, SET IPT(1) = 0
C  FOR IPT(1) GREATER THAN 1, SUCCESSIVE PRINTOUTS WILL OCCUR, DETAILING
C      THE ITERATION PROCESS FOR EACH ITERATION
C  IPT(2) IS NOT USED
C  IPT(3)    SET THIS = 0 FOR A CLOSED SHELL MOLECULE.  IF IPT(3) = 1,
C      ONE ELECTRON WILL BE REMOVED FROM HIGHEST OCCUPIED ORBITAL (RADICAL),
C      IF IPT(3) = 2, A CNDO/2 CALCULATION WILL BE FOR SEPARATE MATRICES
C      FOR ALPHA AND BETA SPINS (FOR FREE RADICALS AGAIN).
C  IPT(4) = 1 FOR CNDO/1 CALCULATIONS, AND = 2 FOR CNDO/2 CALCULATIONS.
```

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```
C  IF(5) IS THE MAXIMUM NUMBER OF ITERATIONS THE PROGRAM WILL PERFORM
C     BEFORE QUITTING. TYPICALLY THIS IS ABOUT 20.
C  Z IS THE ARRAY OF CHARGES ON THE CORE
C  ZS IS THE ARRAY OF SLATER EXPONENTS.
C  BETA IS THE ARRAY OF BETA ZEROS.
C  U IS THE ARRAY OF IONIZATION POTENTIALS.
C  COORD IS THE MATRIX OF CARTESIAN COORDINATES.
C  F IS THE F MATRIX.
C  C IS THE MATRIX OF EIGENVECTORS.
C  P IS THE BOND ORDER, CHARGE DENSITY MATRIX.
C  COS IS THE DIRECTION COSINE MATRIX.
C  PA IS THE ARRAY OF ELECTRON DENSITIES FOR EACH ATOM.
C  V IS THE V-INTEGRAL MATRIX.
C  G IS THE MATRIX OF GAMMA INTEGRALS.
C  E IS THE ENERGY OF THE MOLECULE.
C  ET IS THE ENERGY MATRIX, BREAKING DOWN THE ENERGY INTO ATOMIC
C     AND INTERACTION TERMS.
C  RAD IS THE INTERATOMIC DISTANCES MATRIX.
C  RHO IS THE RHO MATRIX.
C  TAU IS THE TAU MATRIX.
C  PP AND PB ARE ARRAYS USED FOR OPEN SHELL CALCULATIONS ANALAGOUS TO
C     P AND PA IN THE CLOSED SHELL CALCULATION.
C  THE SUBROUTINES HAVE THE FOLLOWING FUNCTIONS
C     PREL MAKES PRELIMINARY CALCULATIONS, CONVERTING THE COORDINATE
C     MATRIX AND THE SLATER DETERMINANT MATRIX INTO COS, RAD, RHO,
C     TAU.
C  OVERL SETS UP THE OVERLAP MATRIX GIVEN ZS, COORD, COS, RAD, RHO, AND
C     TAU.
C  GVAB SETS UP G AND V USING ZS, RAD, RHO, TAU, Z, AND IPT.
C  INITL SETS UP THE INITIAL F MATRIX TO BE DIAGONALIZED.
C  FRST PRINTS OUR COORD, COS, RAD, RHO, TAU, G, F, G, AND V.
C  HDIAG DIAGONALIZES F, GIVING EIGENVECTORS C
C  PM SETS UP THE P AND PA MATRIX GIVEN C, NO, AND IPT(5).
C  SETF SETS UP THE F MATRIX IN TERMS OF THE C OBTAINED ON PREVIOUS IT.
C  INTER PRINTS OUT C, P, PA, AND F.
C  CONVRG SETS KEY = 0 IF C AND P MATRIX ELEMENTS AGREE TO WITHIN .0001.
```

```
C      ENRGY CALCULATES THE ENERGY ELEMENTS AFTER ITERATION IS COMPLETE.
       NT = 4*(N-NH)+NH
       CALL PREL(N,COORD,COS,RAD,ZS,RHO,TAU,NH)
       CALL OVERL(N,NH,ZS,COORD,COS,RAD,S,RHO,TAU)
       CALL GVAB(N,NH,ZS,RAD,S,V,RHO,TAU,Z,IPT)
       CALL INITL(N,NH,BETA,G,S,F)
       IF(IPT(1)) 4,5,4
  4    CALL FRST(N,NH,COORD,COS,RAD,RHO,TAU,S,F,G,V)
  5    CONTINUE
       CALL HDIAG(F,C,U,NT,NR)
       NOC = IPT(5)
       IF(IPT(3)/2-1) 6,6,5
  6    DO 20 I = 1,NOC
       CALL PM(N,NH,NO,C,P,PA,IPT(3))
       CALL SETF(N,NH,P,PA,G,V,BETA,S,Z,F,U,IPT)
       IF(IPT(1)-1) 15,15,14
  14   WRITE (51,101)
       WRITE (51,100) (F(J,J), J = 1,NT)
       CALL INTLR(N,NH,C,P,PA,F)
  15   CONTINUE
       DO 16 J = 1,NT
       DO 16 K = 1,NT
  16   PP(J,K)=P(J,K)
       CALL HDIAG(F,C,U,NT,NR)
       CALL PM(N,NH,NO,C,P,PA,IPT(3))
       CALL COMPR(N,NH,P,PP,KEY)
       IF(KEY) 20,30,20
  20   CONTINUE
  30   CONTINUE
       WRITE (51,101)
       WRITE (51,100) (F(J,J), J = 1,NT)
       CALL SETF(N,NH,P,PA,G,V,BETA,S,Z,F,U,IPT)
       CALL INTER(N,NH,C,P,PA,F)
  35   WRITE (51,104)
       CALL ENRGY(N,NH,P,J,G,BETA,S,Z,RAD,PA,E,ET,V,IPT)
       IF(IPT(1)+1) 39,41,39
```

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```
37    DO 40 J = 1,N
40    WRITE (51,100) (E(J,K), K = J,N)
41    CONTINUE
      WRITE (51,103) I
      WRITE (51,102) ET
50    RETURN
60    CALL PM(N,NH,NO,C,P,PA,0)
      IF(IPT(5)-5) 61,62,61
61    NOI = NO-1
      GO TO 63
62    NOI = NO
63    CALL PM(N,NH,NO1,C,PP,PB,0)
      DO 90 I = 1,NOC
      DO 68 J = 1,N
      PA(J) = 0.5*(PA(J)+PB(J))
68    PB(J) = PA(J)
      CALL SETF(N,NH,P,PA,G,V,BETA,S,Z,F,U,IPT)
      IF(IPT(1)-1) 75,75,74
74    CALL INTER(N,NH,C,P,PA,F)
75    CALL HDIAG(F,C,0,NT,NR)
      IF(IPT(1)-1) 77,77,76
76    WRITE (51,101)
      WRITE (51,100) (F(J,J), J = 1,NT)
77    DO 70 J = 1,NT
      DO 78 K = 1,NT
70    F(J,K) = P(J,K)
      CALL PM(N,NH,NO,C,P,PA,0)
      CALL COMPR(N,NH,F,P,KEY)
      IF(KEY) 80,95,80
80    CALL SETF(N,NH,PP,PB,G,V,BETA,S,Z,F,U,IPT)
      IF(IPT(1)-1) 85,85,84
84    CALL INTER(N,NH,C,PP,PB,F)
85    CALL HDIAG(F,C,0,NT,NR)
      IF(IPT(1)-1) 87,87,86
86    WRITE (51,101)
      WRITE (51,100) (F(J,J), J = 1,NT)
```

```
87  CALL PM(N,NH,NOL,C,PP,PB,0)
90  CONTINUE
95  DO 96 J = 1,NT
    DO 96 K = 1,NT
    F(J,K) = 0.5*(P(J,K)-PP(J,K))
96  P(J,K) = 0.5*(P(J,K)+PP(J,K))
120 PA(J) = PB(J)
    WRITE (51,106)
    DO 97 J = 1,NT
97  WRITE (51,100)  (F(J,K), K = 1,NT)
    WRITE (51,108)
    DO 98 J = 1,NT
98  WRITE (51,100)  (P(J,K), K = 1,NT)
    WRITE (51,107)
    WRITE (51,100)  (PA(J), J = 1,N)
    GO TO 35
100 FORMAT (1H ,10F10.6)
101 FORMAT (17H ORBITAL ENERGIES)
102 FORMAT (1H ,F14.8)
103 FORMAT (1H ,I3,11H ITERATIONS)
104 FORMAT ( 7H ENERGY)
105 FORMAT (24H NORMALIZED EIGENVECTORS)
106 FORMAT (20H SPIN DENSITY MATRIX)
107 FORMAT (3H PA)
108 FORMAT (2H P)
    END

C

    SUBROUTINE INITL(N,NH,BETA,U,S,F)
    DIMENSION BETA(40), U(40), S(40,40), F(40,40)
    NT = 4*(N-NH)+NH
    DO 10 I = 1,NT
10  F(I,I) = U(I)
    DO 20 I = 1,NT
    I1 = I+1
    DO 20 J = I1,NT
```

```
   20   F(I,J) = 0.5*(BETA(I)+BETA(J))*S(I,J)
         F(J,I) = F(I,J)
         RETURN
         END
```

C
```
         SUBROUTINE PM(N,NH,NO,C,P,PA,IPT)
         DIMENSION C(40,40), P(40,40), PA(18)
         NT = 4*(N-NH)+NH
         NOT = N-NH
         DO 10 I = 1,NT
         DO 10 J = 1,NT
         P(I,J) = 0.0
         DO 10 K = 1,NO
   10   P(I,J) = P(I,J)+C(K,I)*C(K,J)
         DO 20 I = 1,NT
         DO 20 J = 1,NT
   20   P(I,J) = 2.0*P(I,J)
         IF(IPT) 21,25,21
   21   DO 24 I = 1,NT
         DO 24 J = 1,NT
   24   P(I,J) = P(I,J) -C(NO,I)*C(NO,J)
   25   DO 30 I = 1,NOT
         ISUB = 4*I-3
         ISUB4 = ISUB+3
         PA(I) = 0.0
         DO 30 J = ISUB,ISUB4
   30   PA(I) = PA(I)+P(J,J)
         NOT1 = NOT+1
         DO 40 I = NOT1,N
         ISUB = I+3*NOT
   40   PA(I) = P(ISUB,ISUB)
         RETURN
         END
```

C
```
         SUBROUTINE SETF(N,NH,P,PA,G,V,BETA,S,Z,F,U,IPT)
         DIMENSION P(40,40), PA(18), G(18,18), V(16,18), BETA(40),
```

```
      DIMENSION B(4,40), F(40,40), Z(18), G(40,40), IPT(5)
      CALL INITL(N,NH,BETA,G,G,F)
      NOT = N-NH
      NS = 4*NOT
      NT = NS+NH
      FIPT = IPT(4)
      DO 10 IM = 1,NT
      IF(IM-NS) 5,5,6
    5 IA = (IM+3)/4
      GO TO 7
    6 IA = IM-3*NOT
    7 F(IM,IM) = F(IM,IM)-(Z(IA)-1.0/FIPT)*G(IA,IA)-(PA(IA)-0.5*P(IM,IM)
     1)*G(IA,IA)
      DO 10 IB = 1,N
      IF(IB-IA) 9,10,9
    9 F(IM,IM) = F(IM,IM)+PA(IB)*G(IA,IB)-V(IA,IB)
   10 CONTINUE
      DO 40 IM = 1,NT
      IM1 = IM+1
      IF(IM-NS) 25,25,26
   25 IA = (IM+3)/4
      GO TO 27
   26 IA = IM-3*NOT
   27 DO 40 IN = IM1,NT
      IF(IN-NS) 35,35,36
   35 IB = (IN+3)/4
      GO TO 37
   36 IB = IN-3*NOT
   37 F(IM,IN) = F(IM,IN)-0.5*P(IM,IN)*G(IA,IB)
   40 CONTINUE
      DO 50 I = 1,NT
      I1 = I+1
      DO 50 J = I1,NT
   50 F(J,I) = F(I,J)
      RETURN
      END
```

60

```
C
      SUBROUTINE COMPR(N,NH,C,P,KEY)
      DIMENSION C(40,40), P(40,40)
      NT = 4*(N-NH)+NH
      DO 10 I = 1,NT
      DO 10 J = 1,NT
      IF(ABSF(C(I,J)-P(I,J))-0.0001) 10,10,20
   10 CONTINUE
      KEY = 0
      GO TO 30
   20 KEY = 1
   30 RETURN
      END
C
      SUBROUTINE ENRGY(N,NH,P,U,G,BETA,S,Z,RAD,PA,E,ET,V,IPT)
      DIMENSION P(40,40), U(40), G(18,18), BETA(40), S(40,40), Z(18),
     1RAD(18,18), PA(18), E(18,18), V(18,18), IPT(5)
      NOT = N-NH
      NM = N-1
      FIPT = IPT(4)
      DO 40 IA = 1,N
      E(IA,IA) = 0.0
      IF(IA-NOT) 15,15,16
   15 IMN = 4*IA-3
      IMX = IMN+3
      GO TO 28
   16 IMN = 3*NOT+IA
      IMX = IMN
   28 DO 40 IM = IMN,IMX
      E(IA,IA) = E(IA,IA) + P(IM,IM)*(U(IM)-(Z(IA)-1.0/FIPT)*G(IA,IA))
      DO 40 IN = IMN,IMX
   40 E(IA,IA) = E(IA,IA)+0.5*(P(IM,IM)*P(IN,IN)
     1 - .5*P(IM,IN)**2)*G(IA,IA)
      DO 140 IA = 1,NM
      IA1 = IA+1
      IF(IA-NOT) 115,115,116
```

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```
115 IMN = 4*IA-3
    IMX = IMN+3
    GO TO 118
116 IMN = 3*NOT+IA
    IMX = IMN
118 DO 140 IB = IA1,N
    IF(IB-NOT) 125,125,126
125 INN = 4*IB-3
    INX = INN+3
    GO TO 128
126 INN = 3*NOT+IB
    INX = INN
128 L(IA,IB) = Z(IA)*Z(IB)/RAD(IA,IB)    PA(IA)*V(IA,IB)
  1 - PA(IB)*V(IB,IA)    + PA(IA)*PA(IB)*G(IA,IB)
    DO 140 IM = IMN,IMX
    DO 140 IN = INN,INX
140 E(IA,IB) = E(IA,IB) + P(IM,IN)*(BETA(IM)+BETA(IN))*S(IM,IN)
  1 - .5*P(IM,IN)**2*G(IA,IB)
    DO 141 I = 1,N
    I1 = I+1
    DO 141 J = I1,N
141 E(J,I) = 0.0
    ET = 0.0
    DO 60 I = 1,N
    DO 60 J = I,N
60  ET = ET+E(I,J)
    RETURN
    END
C
    SUBROUTINE FRST(N,NH,COORD,COS,RAD,RHO,TAU,S,F,G,V)
    DIMENSION COORD(3,18), COS(3,18,18), RAD(18,18), RHO(18,18),
  1 TAU(18,18), S(40,40), F(40,40), G(18,18), V(18,18)
    NT = 4*(N-NH)+NH
    WRITE (51,100)
    DO 10 I = 1,N
10  WRITE (51,120) (COORD(J,I), J = 1,3)
```

```
      WRITE (51,101)
      DO 20 I = 1,3
      DO 20 J = 1,N
   20 WRITE (51,120) (COS(I,J,K), K = 1,N)
      WRITE (51,102)
      DO 25 I = 1,N
   25 WRITE (51,120) (RAD(I,J), J = 1,N)
      WRITE (51,103)
      DO 26 I = 1,N
   26 WRITE (51,120) (RHO(I,J), J = 1,N)
      WRITE (51,104)
      DO 27 I = 1,N
   27 WRITE (51,120) (TAU(I,J), J = 1,N)
      WRITE (51,105)
      DO 30 I = 1,NT
   30 WRITE (51,120) (S(I,J), J = 1,NT)
      WRITE (51,106)
      DO 35 I = 1,N
   35 WRITE (51,120) (G(I,J), J = 1,N)
      WRITE (51,107)
      DO 40 I = 1,N
   40 WRITE (51,120) (V(I,J), J = 1,N)
      WRITE (51,108)
      DO 45 I = 1,NT
   45 WRITE (51,120) (F(I,J), J = 1,NT)
      RETURN
  100 FORMAT (28H COORDINATES IN ATOMIC UNITS)
  101 FORMAT (18H DIRECTION COSINES)
  102 FORMAT (26H DISTANCES IN ATOMIC UNITS)
  103 FORMAT (4H RHO)
  104 FORMAT (4H TAU)
  105 FORMAT (8H OVERLAP)
  106 FORMAT (6H GAMMA)
  107 FORMAT (2H V)
  108 FORMAT (2H F)
  120 FORMAT (1H ,10F11.6)
```

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```
      END
C
      SUBROUTINE INTER(N,NH,C,P,PA,F)
      DIMENSION C(40,40), P(40,40), PA(18), F(40,40)
      NT = (N-NH)*4+NH
      DO 10 I = 1,NT
   10 WRITE (51,120) (C(I,J), J = 1,NT)
      WRITE (51,101)
      DO 20 I = 1,NT
   20 WRITE (51,120) (P(I,J), J = 1,NT)
      WRITE (51,102)
      WRITE (51,120) (PA(I), I = 1,N)
      WRITE (51,103)
      DO 30 I = 1,NT
   30 WRITE (51,120) (F(I,J), J = 1,NT)
      RETURN
  100 FORMAT (2H C)
  101 FORMAT (2H P)
  102 FORMAT (3H PA)
  103 FORMAT (2H F)
  120 FORMAT (1H ,10F11.6)
      END
C
      SUBROUTINE PREL(N,COORD,COS,RAD,ZS,RHO,TAU,NH)
      DIMENSION COORD(3,18), COS(3,18,18), RAD(18,18)
     1ZS(18), RHO(18,18), TAU(18,18)
      DO 5 I = 1,3
      DO 5 J = 1,N
    5 COORD(I,J) = COORD(I,J)/.529167
      DO 10 I = 1,N
      DO 10 J = 1,N
      RAD(I,J) = SQRTF((COORD(1,J)-COORD(1,I))**2
     1 + (COORD(2,J)-COORD(2,I))**2 + (COORD(3,J)-COORD(3,I))**2 )
      DO 10 K = 1,3
   10 COS(K,I,J) = (COORD(K,J)-COORD(K,I))/RAD(I,J)
```

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      DO 30 I = 1,N
      DO 30 J = 1,N
      RHO(I,J) = 0.5*(ZS(I)+ZS(J))*RAD(I,J)
   30 TAU(I,J) = (ZS(I)-ZS(J))/(ZS(I)+ZS(J))
      RETURN
      END
C
      SUBROUTINE OVERL(N,NH,ZS,COORD,COS,RAD,S,RHO,TAU)
      DIMENSION ZS(18), COORD(3,18), COS(3,18,18), RAD(18,18), S(40,40),
     1CA(3,3), CB(3,3), CC(3,3), RHO(18,18), TAU(18,18)
C THIS ROUTINE CALCULATES THE OVERLAP MATRIX S, GIVEN
C     N, THE NUMBER OF ATOMS
C     NH, THE NUMBER OF HYDROGEN ATOMS
C     ZS, THE ARRAY OF SLATER EXPONENTS
C     COORD, THE MATRIX OF CARTESIAN COORDINATES, IN ATOMIC UNITS
C     COS, THE DIRECTION COSINE MATRIX
C     RAD, THE DISTANCE MATRIX, IN ATOMIC UNITS
C     RHO,
C     AND TAU.
C THIS ROUTINE MAKES USE OF SUBROUTINES
C SF(KEY,P,T) WHICH ALSO USES FUNCTION ABF
C THE S MATRIX IS SET UP IN THE BASIS WHICH INCLUDES THE ROW TWO
C ELEMENTS FIRST, THEN THE HYDROGEN ATOMS.  EACH ROW TWO ELEMENT
C IS ARRANGED SEPARATELY, WITH THE BASIS ARRANGED S, PX, PY, PZ FOR EACH.
      NOT = N-NH
      NOT1 = NOT+1
      NS = 4*NOT
      NS1 = NS+1
      NT = NS+NH
      DO 5 I = 1,NT
      DO 5 J = 1,NT
    5 S(I,J) = 0.0
      DO 6 I = 1,NT
    6 S(I,I) = 1.0
C
C CALCULATE PERIOD 2 ATOM OVERLAP INTEGRALS
```

```
C

      DO 20 I = 1,NOT
      II = I+1
      DO 20 J = II,NOT
      ISUB = 4*I-3
      JSUB = 4*J-3
      P = RHO(I,J)
      T = TAU(I,J)
      S(ISUB,JSUB) = SF(4,P,T)
      TA = SF(5,P,T)
      TB = SF(5,P,-T)
      DO 12 K = 1,3
      JK = JSUB+K
      S(ISUB,JK) = TA*COS(K,J,I)
      IK = ISUB+K
   12 S(IK,JSUB) = TB*COS(K,I,J)
      DO 14 K = 1,3
      DO 14 L = 1,3
      CA(K,L) = 0.0
      CB(K,L) = 0.0
   14 CC(K,L) = 0.0
      CB(1,1) = SF(6,P,T)
      CB(2,2) = SF(7,P,T)
      CB(3,3) = CB(2,2)
      DEN = SQRTF(COS(2,I,J)**2+COS(3,I,J)**2)
      CA(1,1) = COS(1,I,J)
      IF(DEN-.000001) 16,16,18
   16 CA(2,2) = 1.0
      CA(3,3) = 1.0
      GO TO 19
   18 CA(1,2) = COS(2,I,J)
      CA(1,3) = COS(3,I,J)
      CA(2,2) = COS(3,I,J)/DEN
      CA(2,3) = -COS(2,I,J)/DEN
      CA(3,1) =-(CA(1,2)**2+CA(1,3)**2)/DEN
      CA(3,2) = CA(1,1)*CA(1,2)/DEN
```

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```
      CA(3,3) = CA(1,1)*CA(1,3)/DEN
   19 DO 15 K = 1,3
      DO 15 L = 1,3
   15 CC(K,L) = CA(K,L)
      DO 17 K = 1,3
      DO 17 L = 1,3
      IK = ISUB+K
      IL = JSUB+L
      S(IK,IL) = 0.0
      DO 17 M = 1,3
   17 S(IK,IL) = S(IK,IL)+CA(M,K)*CB(M,M)*CC(M,L)
   20 CONTINUE
C
C     CALCULATE PERIOD 2 - HYDROGEN OVERLAP INTEGRALS
C
      DO 40 I = 1,NOT
      I1 = 4*I-3
      I2 = I1+1
      I3 = I2+1
      I4 = I3+1
      DO 40 J = NOT1,N
      JSUB = 3*NOT+J
      P = RHO(I,J)
      T = TAU(I,J)
      S(I1,JSUB) = SF(2,P,T)
      SFS = SF(3,P,T)
      S(I2,JSUB) = SFS*COS(1,I,J)
      S(I3,JSUB) = SFS*COS(2,I,J)
   40 S(I4,JSUB) = SFS*COS(3,I,J)
C
C     CALCULATE HYDROGEN OVERLAP INTEGRALS
C
      NB = 3*NOT
      DO 60 I = NOT1,N
      I1 = I+1
      ISUB = NB+I
```

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```
      DO 60 J = I1,N
      JSUB = NB+J
   60 S(ISUB,JSUB) = SF(1,RHO(I,J),TAU(I,J))
      DO 80 I = 1,NT
      I1 = I+1
      DO 80 J = I1,NT
   80 S(J,I) = S(I,J)
      RETURN
      END
C
      FUNCTION SF(KEY,P,T)
      TS = ABSF(T)
      IF(ABSF(T)-0.000001) 2,2,1
    1 GO TO (10,20,30,40,50,60,70) KEY
    2 GO TO (110,120,130,140,150,160,170) KEY
C
   1S1S, 1S2PS, 1S2S, 2S2S, 2S2PS, 2PS2PS, 2PP2PP
   10 SF = (P**3/4.0)*SQRTF((1.0-T*T)**3)*(ABF(1,2,P,TS)*ABF(2,0,P,TS) -
     1 ABF(1,0,P,TS)*ABF(2,2,P,TS))
      RETURN
   20 SF = (P**4/8.0)*SQRTF((1.0+T)**3*(1.0-T)**5/3.0)*(ABF(1,3,P,T)*
     1ABF(2,0,P,T) - ABF(1,2,P,T)*ABF(2,1,P,T) - ABF(1,1,P,T)*ABF(2,2,P,
     2T) + ABF(1,0,P,T)*ABF(2,3,P,T))
      RETURN
   30 SF = (P**4*SQRTF((1.0+T)**3*(1.0-T)**5/8.0)*( -ABF(1,3,P,T)*ABF(
     1 2,1,P,T) + ABF(1,2,P,T)*ABF(2,0,P,T) + ABF(1,1,P,T)*ABF(2,3,P,T)
     2 - ABF(1,0,P,T)*ABF(2,2,P,T))
      RETURN
   40 SF = (P**5*SQRTF((1.0-T*T)**5)/48. ) *  (ABF(1,4,P,TS)*ABF(2,0,P,TS
     1) - 2.0*ABF(1,2,P,TS)*ABF(2,2,P,TS) + ABF(1,0,P,TS)*ABF(2,4,P,TS))
      RETURN
   50 SF = (P**5*SQRTF((1.0-T**2)**5/3.0)/16.0)*
     1(ABF(1,3,P,T)*(ABF(2,0,P,T)-ABF(2,2,P,T)) +
     2ABF(1,1,P,T)*(ABF(2,4,P,T)-ABF(2,2,P,T)) +
     3ABF(2,1,P,T)*(ABF(1,2,P,T)-ABF(1,4,P,T)) +
     4ABF(2,3,P,T)*(ABF(1,2,P,T)-ABF(1,0,P,T)))
      RETURN
```

```
  60 SF = (P**5/16.0)*SQRTF((1.0-T*T)**5) *
    1(ABF(2,2,P,TS)*(ABF(1,0,P,TS) + ABF(1,4,P,TS)) -
    2ABF(1,2,P,TS)*(ABF(2,0,P,TS) + ABF(2,4,P,TS)))
     RETURN
  70 SF = (P**5/32.0) * SQRTF((1.0-T*T)**5) *
    1(ABF(1,4,P,TS)*(ABF(2,0,P,TS)-ABF(2,2,P,TS)) +
    2ABF(1,2,P,TS)*(ABF(2,4,P,TS)-ABF(2,0,P,TS)) +
    3ABF(1,0,P,TS)*(ABF(2,2,P,TS)-ABF(2,4,P,TS)))
     RETURN
 110 SF = (P**3/6.0)*(3.0*ABF(1,2,P,T)-ABF(1,0,P,T))
     RETURN
 120 SF = (P**4/(12.0*SQRTF(3.0)))*(3.0*ABF(1,3,P,T)-ABF(1,1,P,T))
     RETURN
 130 SF = (P**4/12.0)*(3.0*ABF(1,2,P,T) ABF(1,0,P,T))
     RETURN
 140 SF = (P**5/360.0)*(15.0*ABF(1,4,P,T)-10.0*ABF(1,2,P,T)+3.0*ABF(1,0
    1,P,T))
     RETURN
 150 SF = (P**5/(60.0*SQRTF(3.0)))*(5.0*ABF(1,3,P,T)-ABF(1,1,P,T))
     RETURN
 160 SF = (P**5/120.0)*(5.0*ABF(1,4,P,T)-18.0*ABF(1,2,P,T) +
    15.0*ABF(1,0,P,T))
     RETURN
 170 SF = (P**5/120.0)*(5.0*ABF(1,4,P,T)-6.0*ABF(1,2,P,T) +
    1ABF(1,0,P,T))
     RETURN
     END
C
     FUNCTION ABF(KAB,KP,P,T)
     DIMENSION FACT(10), DUM(2)
     EQUIVALENCE (DUM(2),FACT(1))
     KP1 = KP+1
     IF(IFBF-12345) 10,20,10
  10 DUM(2) = 1.0
     DO 12 I = 1,10
     FI = I
```

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```
   12 FACT(I) = FACT(I-1)*FI
      IFBF = 12345
   20 ABF = 0.0
      GO TO (30,130) KAB
   30 DO 40 M = 1,KP1
      KM1 = KP-M+1
   40 ABF = ABF+1.0/(P**M*FACT(KM1))
      ABF = ABF*FACT(KP)*EXPF(-P)
      RETURN
  130 BA = 0.0
      BB = 0.0
      PT = P*T
      DO 140 M = 1,KP1
      KM = KP-M
      KM1 = KP-M+1
      ABF = 1.0/((P*T)**M*FACT(KM1))
      BA = BA+ABF
  140 BB = BB+(-1.0)**KM*ABF
      EPT = EXPF(-PT)
      ABF = -EPT*FACT(KP)*BA-FACT(KP)*BB/EPT
      RETURN
      END
C
      SUBROUTINE GVAB(N,NH,ZS,RAD,G,V,RHO,TAU,Z,IPT)
      DIMENSION ZS(18), RAD(18,18), G(18,18), V(18,18), RHO(18,18),
     1TAU(18,18), IPT(5), Z(18)
      NOT = N-NH
      NOT1 = NOT+1
      DO 10 I = 1,N
      DO 10 J = 1,N
      G(I,J) = 0.0
   10 V(I,J) = 0.0
      DO 20 I = 1,NOT
      I1 = I+1
      DO 20 J = I1,NOT
      G(I,J) = GF(3,RHO(I,J),TAU(I,J),RAD(I,J))
```

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      G(J,I) = G(I,J)
      RD = RAD(I,J)
      P = ZS(I)*RD
      V(I,J) = VF(2,P,RD)*Z(J)
      P = ZS(J)*RD
   20 V(J,I) = VF(2,P,RD) *Z(I)
      DO 40 I = 1,NOT
      DO 40 J = NOT1,N
      RD = RAD(I,J)
      G(I,J) = GF(2,RHO(I,J),-TAU(I,J),RD)
      G(J,I) = G(I,J)
      P = ZS(I)*RD
      V(I,J) = VF(2,P,RD)*Z(J)
      P = ZS(J)*RD
   40 V(J,I) = VF(1,P,RD)*Z(I)
      DO 60 I = NOT1,N
      I1 = I+1
      DO 60 J = I1,N
      G(I,J) = GF(1,RHO(I,J),TAU(I,J),RAD(I,J))
      G(J,I) = G(I,J)
      RD = RAD(I,J)
      P = ZS(I)*RD
      V(I,J) = VF(1,P,RD)*Z(J)
      P = ZS(J)*RD
   60 V(J,I) = VF(1,P,RD)*Z(I)
      DO 80 I = 1,NOT
   80 G(I,I) = 0.36328125*ZS(I)
      DO 81 I = NOT1,N
   81 G(I,I) = 0.625*ZS(I)
      IF(IPT(4)-2) 90,85,90
   85 DO 87 I = 1,N
      DO 87 J = 1,N
   87 V(I,J) = Z(J)*G(I,J)
      DO 88 I = 1,N
   88 V(I,I) = 0.0
   90 RETURN
```

```
      END
C
      FUNCTION GF(KEY,P,T,R)
      IF(ABSF(T)-0.000001) 1,1,2
    1 GO TO (110,120,130) KEY
    2 AK = 0.5*(T+1.0/T)
      PA = (1.0+T)*P
      PB = (1.0-T)*P
      GO TO (10,20,30) KEY
   10 GF = (1.0-(1.0-AK)**2*((2.0+AK)/4.   PA/4.0)*EXPF(-2.0*PA)  -
     1 (1.0+AK)**2*((2.0-AK)/4.0+PB/4.0)*EXPF(-2.0*PB))/R
      GO TO 100
   20 GF = (1.0-(1.0-AK)**3*((1.0-5.0*AK   4.0*AK**2)/16.0-AK*PA/8.0)*
     1EXPF(-2.0*PA)  -  (1.0+AK)**2*((15.0  22.0*AK+15.0*AK**2-4.0*AK**3)
     2/16.0+3.0*(3.0-3.0*AK+AK**2)*PB/8.   (2.0-AK)*PB**2/4.0+PB**3/12.)*
     3EXPF(-2.0*PB))/R
      GO TO 100
   30 GF = (1.0-(1.0-AK)**3*((8.-AK-27.0*AK**2-30.0*AK**3-10.0*AK**4)/
     1 16.0+(11.0-19.0*AK-44.0*AK**2-20.  *AK**3)*PA/32.0+(1.0-5.0*AK
     2 -4.0*AK**2)*PA**2/16.0-AK*PA**3/24.0)*EXPF(-2.0*PA)  -  (1.0+AK)**3
     3*((8.+AK-27.0*AK**2+30.0*AK**3-10.  *AK**4)/16.0+(11.0+19.0*AK-44.0
     4*AK**2+20.0*AK**3)*PB/32.0+(1.0+5.  *AK-4.0*AK**2)*PB**2/16.0
     5+AK*PB**3/24.)*EXPF(-2.0*PB))/R
      GO TO 100
  110 GF = (1.0-(1.0+11.0*P/8.0+3.0*P**2/4.0+P**3/6.0)*EXPF(-2.0*P))/R
      GO TO 100
  120 GF = (1.0-(1.0+25.0*P/16.0+9.0*P**2/8.0+23.0*P**3/48.0+P**4/8.0
     1+P**5/60.0)*EXPF(-2.0*P))/R
      GO TO 100
  130 GF = (1.0-(1.0+419.0*P/256.0+163.0*P**2/128.0+119.0*P**3/192.0
     1+5. *P**4/24.0+P**5/20.0+P**6/120.  P**7/1260.0)*EXPF(-2.0*P))/R
  100 RETURN
      END
C
      FUNCTION VF(KEY,P,R)
      GO TO (10,20) KEY
```

```
   10 VF = (1.0-(1.0+P) *EXPF(-2.0*P))/R
      GO TO 100
   20 VF = (1.0-(1.0+1.5*P+P**2+P**3/3.0)*EXPF(-2.0*P))/R
  100 RETURN
      END
C
      SUBROUTINE HDIAG(H,U,IEGEN,N,NR)
      DIMENSION H(40,40), ROOT(40), U(40,40), B(40,5)
      IC = 0
      DO 10 J = 1,N
      DO 10 I = 1,J
      IC = IC+1
   10 H(IC) = H(I,J)
      CALL GIVENS(N,N,H,B,ROOT,U)
      IC = 0
      DO 30 I = 1,N
      DO 30 J = 1,N
      IC = IC+1
   30 H(J,I) = U(IC)
      DO 40 I = 1,N
      DO 40 J = 1,N
      U(I,J) = H(J,I)
   40 H(J,I) = 0.0
      DO 50 I = 1,N
   50 H(I,I) = ROOT(I)
      RETURN
      END
      SUBROUTINE GIVENS (NX,NROOTX,A,B,ROOT,VECT)                      0003
                                                                         4
C                                                                        5
C     EIGENVALUES AND EIGENVECTORS BY GIVENS METHOD.                  0006
C     - - - -                                                            7
C                                                                        8
C     CALCULATES EIGENVALUES AND EIGENVECTORS OF REAL SYMMETRIC MATRIX 0009
C     BY THE MODIFIED GIVENS METHOD.  THE PARAMETERS ARE...            000
C     NX    ORDER OF MATRIX                                           0010
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C     NROOTX  NUMBER OF ROOTS WANTED.  MOST NEGATIVE ROOTS ARE          0011
C             FOUND FIRST.  IF NO VECTORS ARE WANTED, MAKE THIS         0012
C             NUMBER NEGATIVE.                                          0013
C     A       MATRIX STORED BY COLUMNS IN PACKED UPPER TRIANGULAR       0014
C             FORM, I.E. OCCUPYING NX*(NX+1)/2 CONSECUTIVE              0015
C             LOCATIONS.                                                0016
C     ROOT    ARRAY TO HOLD THE EIGENVALUES.  MUST BE AT LEAST          0017
C             NROOTX CELLS LONG.                                        0018
C     VECT    EIGENVECTOR ARRAY.  EACH COLUMN WILL HOLD AN              0019
C             EIGENVECTOR FOR THE CORRESPONDING ROOT.  MUST BE          0020
C             AT LEAST NX*NROOTX CELLS LONG, UNLESS NO VECTORS          0021
C             ARE REQUESTED (NEGATIVE NROOTX).  IN THIS LATTER          0022
C             CASE, THE ARGUMENT VECT IS JUST A DUMMY, AND THE          0023
C             STORAGE IS NOT USED.                                      0024
C                                                                        25
C     THE ARRAYS A AND B ARE DESTROYED BY THE COMPUTATION.  THE RESULTS 0026
C     APPEAR IN ROOT AND VECT.                                          0027
C                                                                        28
C     THE ORIGINAL REFERENCE TO THE GIVENS TECHNIQUE IS IN OAK RIDGE    0029
C     REPORT NUMBER ORNL 1574 (PHYSICS), BY WALLACE GIVENS.             0030
C     THE METHOD AS PRESENTED IN THIS PROGRAM CONSISTS OF FOUR STEPS,   0031
C     ALL MODIFICATIONS OF THE ORIGINAL METHOD...                      0032
C     FIRST, THE INPUT MATRIX IS REDUCED TO TRIDIAGONAL FORM BY THE     0033
C     HOUSEHOLDER TECHNIQUE (J. H. WILKINSON, COMP. J. 3, 23 (1960)).   0034
C     THE ROOTS ARE THEN LOCATED BY THE STURM SEQUENCE METHOD (J. M.    0035
C     ORTEGA, J.ACM 7, 260 (1960)).  THE VECTORS OF THE TRIDIAGONAL     0036
C     FORM ARE THEN EVALUATED (J. H. WILKINSON, COMP. J. 1, 90 (1958)), 0037
C     AND LAST THE TRIDIAGONAL VECTORS ARE ROTATED TO VECTORS OF THE    0038
C     ORIGINAL ARRAY (FIRST REFERENCE).                                 0039
C                                                                        40
C     VECTORS FOR DEGENERATE (OR NEAR-DEGENERATE) ROOTS ARE FORCED      0041
C     TO BE ORTHOGONAL, USING A METHOD SUGGESTED BY B. GARBOW, ARGONNE  0042
C     NATIONAL LABS (PRIVATE COMMUNICATION, 1964).  THE GRAM-SCHMIDT    0043
C     PROCESS IS USED FOR THE ORTHOGONALIZATION.                        0044
C                                                                        45
C                                                                        46
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      DIMENSION B(NX,5), A(1), ROOT(1), VECT(NX,NROOTX)              0047
      DATA (KILLBIT = 7777777777777776B),(ETA = 1.0E-10)            0048
                                                                    49
      N = NX                                                        0050
      NROOT = XABSF(NROOTX)                                         0051
      GO TO (1010,105) N                                            0052
 1010 ROOT = A                                                      0053
      GO TO 807                                                     0054
  105 CONTINUE                                                      0055
                                                                    56
C     NSIZE    NUMBER OF ELEMENTS IN THE ARRAY                      0057
      NSIZE = N*(N+1)/2                                             0058
      NM1 = N - 1                                                   0059
      NM2 = N - 2                                                   0060
                                                                    61
C     TRIDIAGONALIZATION OF SYMMETRIC MATRIX                        0062
C     - - - - -                                                     63
                                                                    64
      ID = 0                                                        0065
      IA = 1                                                        0066
                                                                    67
      DO 200  J=1,NM2                                               0068
C     J       COUNTS ROWS OF A-MATRIX TO BE DIAGONALIZED           0069
C     IA      START OF NON-CODIAGONAL ELEMENTS IN THE ROW          0070
C     ID      POSITION OF DIAGONAL ELEMENT ON ROW BEING CODIAGONALIZED  0071
      IA = IA+J+2                                                   0072
      ID = ID + J                                                   0073
      JUMP = J+1                                                    0074
                                                                    75
C     SUM SQUARES OF NON-CODIAGONAL ELEMENTS IN ROW J              0076
      SUM = 0.0                                                     0077
      DO 100  I=IA,NSIZE,JUMP                                       0078
      SUM = SUM + A(I)**2                                           0079
      JUMP = JUMP + 1                                               0080
  100 TEMP = A(ID+J)                                                0081
      IF(SUM) 110,120,110
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```
C     NO TRANSFORMATION NECESSARY IF ALL THE NON-CODIAGONAL
C     ELEMEMTS ARE ZERO.
120   B(J) = TEMP
      A(ID+J) = 0.0
      GO TO 200

C     NOW COMPLETE THE SUM OF OFF-DIAGONAL SQUARES
110   SUM = SQRTF(SUM+ TEMP**2)

C     NEW CODIAGONAL ELEMENT
      B(J) = -SIGNF(SUM,TEMP)

C     FIRST NON-ZERO ELEMENT OF THIS W-VECTOR
      JUMP = J + 1
      B(JUMP,2) = SQRTF((1.0 + ABSF(TEMP)/SUM)/2.0)

C     FORM REST OF THE W-VECTOR ELEMENTS
      TEMP = SIGNF(0.5/(B(JUMP,2)*SUM),TEMP)
      DO 130  I=IA,NSIZE,JUMP
      JUMP = JUMP + 1
130   B(JUMP,2) = A(I)*TEMP

C     FORM P-VECTOR AND SCALAR.  P-VECTOR = A-MATRIX*W-VECTOR.
C     SCALAR = W-VECTOR*P-VECTOR.

C     AK = 0.0
C     IC    LOCATION OF NEXT DIAGONAL ELEMENT
      IC = ID + J + 1
      J1 = J + 1

      DO 190  I=J1,N
      JJ = IC
      TEMP = 0.
      DO 180  II=J1,N
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C          I      RUNS OVER THE NON-ZERO P-ELEMENTS               0119
C          II     RUNS OVER ELEMENTS OF W-VECTOR                  0120
           TEMP = TEMP + B(II,2)*A(JJ)                            0121
C                                                                  122
C     CHANGE INCREMEMTING MODE AT THE DIAGONAL ELEMENTS           0123
      IF(II-I) 210,140,140                                        0125
140   JJ = JJ + II                                                0126
      GO TO 180                                                   0127
210   JJ = JJ + 1                                                 0128
180   CONTINUE                                                     129
C     BUILD UP THE K-SCALAR (AK)                                  0130
      AK = AK + TEMP*B(I,2)                                       0131
      B(I) = TEMP                                                 0132
C     MOVE IC TO TOP OF NEXT A-MATRIX -ROW-                       0133
190   IC = IC + I                                                 0134
C                                                                  135
C     FORM THE Q-VECTOR                                           0136
      DO 150  I=J1,N                                              0137
150   B(I) = B(I) - AK*B(I,2)                                     0138
C                                                                  139
C     TRANSFORM THE REST OF THE A-MATRIX                          0140
C          START-1 OF THE REST OF THE A-MATRIX                    0141
      JJ = ID + J                                                 0142
C     MOVE W-VECTOR INTO THE OLD A-MATRIX LOCATIONS TO SAVE SPACE 0143
C          I  RUNS OVER THE SIGNIFICANT ELEMENTS OF THE W-VECTOR  0144
      DO 160  I=J1,N                                              0145
      A(JJ) = B(I,2)                                              0146
                                                                   147
      DO 170  II=J1,I                                             0148
      JJ = JJ + 1                                                 0149
170   A(JJ) = A(JJ) - 2.0*(B(I)*B(II,2)   B(I,2)*B(II))           0150
160   JJ = JJ + J                                                 0151
200   CONTINUE                                                    0152
C                                                                  153
C     MOVE LAST CODIAGONAL ELEMENT OUT INTO ITS PROPER PLACE      0154
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```
      B(N-1) = A(NSIZE-1)
      A(NSIZE -1) = 0.0
C
C     SHIFT ALL CODIGONAL ELEMENTS DOWN ONE PLACE TO TAKE ADVANTAGE
C     OF FORWARD INDEXING (I.E. FIRST CODIAGONAL ELEMENT MUST BE ZERO).
      DO 205 J=1,NM1
  205 B(N+1-J) = B(N-J)
      B(1) = 0.
C
C     STURM SEQUENCE ITERATION TO OBTAIN ROOTS OF TRIDIAGONAL FORM
C     -  -  -  -  -
C
C     MOVE DIAGONAL ELEMENTS INTO SECOND N ELEMENTS OF B-VECTOR.
C     THIS IS A MORE CONVENIENT INDEXING POSITION.
C     ALSO, PUT SQUARE OF CODIAGONAL ELEMENTS IN THIRD N ELEMENTS
C     OF B-VECTOR FOR USE IN STURM SEQUENCE EVALUATION.
C     AT THE SAME TIME, COMPUTE THE NORM OF THE MATRIX.
      ANORM = 0.
      JUMP = 1
      DO 300  J=1,N
      B(J,3) = B(J)**2
      B(J,2) = A(JUMP)
      ANORM = ANORM + 2.0*B(J,3) + A(JUMP)**2
  300 JUMP = JUMP + J + 1
C
C     NORM OF MATRIX AND SMALL CONVERGENCE LIMIT.
      ANORM = SQRTF(ANORM)
      DELTA = ANORM*ETA
      IF (DELTA)  320,1001
C     ROOT(I) HOLDS LOWER LIMIT OF EIGENVALUE I.
C     B(I,4) HOLDS UPPER LIMIT OF EIGENVALUE I.
  320 DO 310  I=1,NROOT
```

```
310       ROOT(I) = -ANORM                                           0191
          B(I,4) = +ANORM                                            0192
C     ISOLATE THE ROOTS.                                             0193
          DO 330  I=1,NROOT                                          0194
C     IMPROVE THE TRIAL ROOT                                         0195
500       TRIAL = (ROOT(I)+B(I,4))*0.5                               0196
          IF((B(I,4)-ROOT(I))-DELTA) 330,330,350

C     FORM STURM SEQUENCE.                                           198
C     NOMATCH IS ONE GREATER THAN THE NUMBER OF ROOTS LESS THAN      0199
C     THE TRIAL VALUE.                                               0200
350       NOMATCH = 1                                                0201
          F1 = 1.0                                                   0202
          DO 360  J=1,N                                              0203
          DIAG = B(J,2) - TRIAL                                      0204
                                                                     0205
                                                                     206
420       IF (B(J)) 410,420                                          0207
          FO = DIAG*SIGNF(1.0,F1)                                    0208
          GO TO 400                                                  0209
                                                                     210
410       FO = DIAG*F1                                               0211
          IF (B(J-1)) 430,440                                        0212
440       FO = FO - B(J,3)*SIGNF(1.0,F2)                             0213
          GO TO 400                                                  0214
                                                                     215
430       FO = FO - B(J,3)*F2                                        0216
                                                                     217
400       IF (FO) 450,460,470                                        0218
460       FO = SIGNF(0.0,F1)                                         0219
          GO TO 510                                                  0220
                                                                     221
480   IF(FO*SIGNF(1.0,F1)) 520,520,510
470       IF (F1) 520,480,510                                        0223
                                                                     224
450       IF (F1) 510,480,520                                        0225
520       NOMATCH = NOMATCH + 1                                      0226
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510      F2 = F1
         F1 = F0
360      CONTINUE
C        ESTABLISH NEW BOUNDS FOR REMAINING ROOTS.
         DO 540  J=1,NROOT
         IF(J-NOMATCH) 600,610,510
C
C        NEW UPPER BOUND FOR THIS ROOT
600      B(J,4) = TRIAL
         GO TO 540
C
C        NEW LOWER BOUND FOR THIS ROOT
610      IF(ROOT(J)-TRIAL) 539,500,500
539      ROOT(J) = TRIAL
540      CONTINUE
         GO TO 500
330      CONTINUE
C
C        EIGENVECTORS OF CODIAGONAL FORM
C        - - - - -
807      CONTINUE
C        QUIT NOW IF NO VECTORS WERE REQUESTED.
         IF(NROOTX) 1002,808,808
808      NRSIZE = N*NROOT
C
C        SET INITIAL VALUES TO VECTORS TO TRY TO SOLVE THE
C        DEGENERACY PROBLEM FOR MOST CASES.
         VECT(1) = 1.0
         GO TO (1002,806) N
806      DO 805  I=2,NRSIZE
```

```
805    VECT(I) = VECT(I-1) + 0.013125901                              0262
C      DON-T GET EXCITED.  THE CONSTANT IS JUST A FACTOR TO TRY TO    0263
C      DESTROY CYCLES IN THE STARTING VECTORS.  THIS HELPS OUT THE    0264
C      ALGORITHM IN SOME CASES WITH MANY DEGENERACIES.                0265
                                                                       266
       DO 700  I=1,NROOT                                              0267
       AROOT = ROOT(I)                                               0268
                                                                       269
C      TEST FOR REPEATED ROOT (WITHIN A LIMIT OF DELTA)              0270
       GO TO (710,715) I                                             0271
715    IF((AROOT-ROOT(I-1))-DELTA) 720,71 ,710                       0273
710    IA = -1                                                       2274
720    IA = IA + 1                                                    275
                                                                      0276
       ELIM1 = A(1) - AROOT                                          0277
       ELIM2 = B(2)                                                  0278
       JUMP = 1                                                       279
                                                                      0280
       DO 750  J=1,NM1                                               0281
       JUMP = JUMP+J+1                                                282
                                                                      0283
C      GET THE CORRECT PIVOT EQUATION FOR THIS STEP                   285
       IF(ABSF(ELIM1)-ABSF(B(J+1))) 760,755,755                      0286
                                                                    
C      FIRST (ELIM1) EQUATION IS THE PIVOT THIS TIME                 0289
755    IF(ELIM1) 757,756,757                                         0290
756    ELIM1 = DELTA                                                 0291
757    B(J,2) = ELIM1                                                 292
       B(J,3) = ELIM2                                                0293
       B(J,4) = 0.                                                   0294
       TEMP = B(J+1)/ELIM1                                            295
                                                                      0296
C      SAVE FACTOR FOR THE SECOND ITERATION.  MARK IT AS CASE 1
       B(J,5) = TEMP.AND.KILLBIT

       ELIM1 = A(JUMP)-AROOT - TEMP*ELIM2
```

```
      ELIM2 = B(J+2)
      GO TO 750
C
  760 SECOND EQUATION IS THE PIVOT THIS TIME.
      B(J,2) = B(J+1)
      B(J,3) = A(JUMP) - AROOT
      B(J,4) = B(J+2)
      TEMP = ELIM1/B(J+1)
C
      SAVE FACTOR FOR SECOND ITERATION.  MARK IT AS CASE 2
      B(J,5) = TEMP.OR.1B
C
      ELIM1 = ELIM2 - TEMP*B(J,3)
      ELIM2 = -TEMP*B(J+2)
  750 CONTINUE
      IF(ELIM1) 752,751,752
  751 ELIM1 = DELTA
  752 B(N,2) = ELIM1
      B(N,3) = B(N,4) = 0.
      B(N-1,4) = 0.
      ITER = 1
      IF(IA) 800,790,800
C
      BACK SUBSTITUTE TO GET THIS VECTOR
  790 L = N + 1
      DO 780 J=1,N
      L = L - 1
  780 VECT(L,I) =(VECT(L,I) - VECT(L+1,I)*B(L,3) - VECT(L+2,I)*
     X            B(L,4))/B(L,2)
      GO TO (820,800) ITER
C
      SECOND ITERATION.  (BOTH ITERATIONS FOR REPEATED-ROOT VECTORS)
  820 ITER = ITER + 1
```

82

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890      ELIM1 = VECT(1,I)
         DO 830   J=1,NM1                                          0332
         TEMP = B(J,5).AND.1B                                      0333
         IF (TEMP)  840,850                                        0334
                                                                   0335
C        CASE ONE.                                                 336
850      VECT(J,I) = ELIM1                                         0337
         ELIM1 = VECT(J+1,I) - ELIM1*B(J,5)                        0338
         GO TO 830                                                 0339
                                                                   0340
C        CASE TWO.                                                 341
840      VECT(J,I) = VECT(J+1,I)                                   0342
         TEMP = B(J,5).AND.KILLBIT                                 0343
         ELIM1 = ELIM1 - VECT(J+1,I)*TEMP                          0344
                                                                   0345
830      CONTINUE                                                  346
         VECT(N,I) = ELIM1                                         0347
         GO TO 790                                                 0348
                                                                   0349
C        ORTHOGONALIZE THIS REPEATED-ROOT VECTOR TO OTHERS WITH THIS ROOT   350
C        IF THIS SECTION IS ENTERED WITH IA=0, THE SECTION IS A NO-OP.      0351
800      DO 860   J1 =1,IA                                         0352
         K = I - J1                                                0353
         TEMP = 0.                                                 0354
.                                                                  0355
                                                                   356
         DO 870   J=1,N                                            0357
870      TEMP = TEMP + VECT(J,I)*VECT(J,K)                         0358
.                                                                  359
         DO 880   J=1,N                                            0360
880      VECT(J,I) = VECT(J,I) - TEMP*VECT(J,K)                    0361
860      CONTINUE                                                  0362
                                                                   363
885      GO TO (890,900) ITER                                      0364
                                                                   365
C        NORMALIZE THE VECTOR                                      0366
900      TEMP = 0.                                                 0367
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             DO 910   J=1,N                                            0368
910          TEMP = TEMP + VECT(J,I)**2                                0369
             TEMP = 1.0/SQRTF(TEMP)                                    0370
                                                                       371
             DO 920   J=1,N                                            0372
             VECT(J,I) = VECT(J,I)*TEMP                                0373
                                                                       374
C            IF VECTOR ELEMENT IS VERY SMALL, SET IT TO ZERO.          0375
             IF(ABSF(VECT(J,I))-ETA) 919,920,92
919          VECT(J,I) = 0.0
920          CONTINUE                                                  0377
                                                                       378
700          CONTINUE                                                  0379
                                                                       380
                                                                       381
                                                                       382
C            ROTATE CODIAGONAL VECTORS INTO VECTORS OF ORIGINAL ARRAY  0383
C            -     -     -     -     -                                  0384
                                                                       385
C            LOOP OVER ALL THE TRANSFORMATION VECTORS                  0386
             JUMP = NSIZE - (N+1)                                      0387
             IM = NM1                                                  0388
             DO 950   I=1,NM2                                          0389
             J1 = JUMP                                                 0390
                                                                       391
C            MOVE A TRANSFORMATION VECTOR OUT INTO BETTER INDEXING POSITION.  0392
             DO 955   J=IM,N                                           0393
             B(J,2) = A(J1)                                            0394
955          J1 = J1 + J                                               0395
                                                                       396
C            MODIFY ALL REQUESTED VECTORS.                             0397
             DO 960   K=1,NROOT                                        0398
             TEMP = 0.                                                 0399
                                                                       400
C            FORM SCALAR PRODUCT OF TRANSFORMATION VECTOR WITH EIGENVECTOR  0401
             DO 970   J=IM,N                                           0402
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970      TEMP = TEMP + B(J,2)*VECT(J,K)                              0403
         TEMP = TEMP + TEMP                                          0404
         DO 980  J=IM,N                                              0405
980      VECT(J,K) = VECT(J,K) - TEMP*B(J,2)                         0406
960      CONTINUE                                                    0407
         JUMP = JUMP - IM                                            0408
950      IM = IM - 1                                                 0409
                                                                      410
1002     CONTINUE                                                    0411
1001     RETURN                                                      0412
         END                                                         0413
C
         SUBROUTINE INPUT(N,NH,NO,IPT,ISTP,AL,TH,PH,BONDL,Z,ZS,BETA,U,COORD
        1, AW)
         DIMENSION IPT(5), ISTP(18),  AL(18),  TH(18),  PH(18),  BONDL(18),
        1Z(18), ZS(18), BETA(40), U(40), COORD(3,18), SZ(9), SZS(9),
        2SBETA(9), SUS(2,9), SUP(2,9), SAW(9), NOAT(18),
        3AW(18), ROX(18,3,3), IST(18), CE(3,18)
C THIS ROUTINE READS IN DATA AND ARRANGES IT SUCH THAT CNDO MAKES USE OF IT.
C N IS THE NUMBER OF ATOMS READ IN. INITIALLY DUMMY ATOMS MAY BE READ IN
C    WITH THEIR ATOMIC NUMBER = 0.  THEY WILL BE LATER REMOVED IN A
C    SUBROUTINE.  N IS THUS INITIALLY SET EQUAL TO THE NUMBER OF ATOMS,
C NO IS THE NUMBER OF ORBITALS OCCUPIED.
C IPT IS AN ARRAY OF OPTIONS - SEE CNDO
C ISTP IS THE ARRAY OF STARTING POINTS USED IN CONSTRUCTING CARTESIAN
C    COORDINATES FROM BOND ANGLES AND DISTANCES.
C AL IS THE ARRAY OF ANGLES ALPHA
C TH IS THE ARRAY OF ANGLES THETA
C PH IS THE ARRAY OF ANGLES PHI
C BONDL IS THE ARRAY OF BOND LENGTHS
C Z IS THE ARRAY OF CORE CHARGES
C ZS IS THE ARRAY OF SLATER EXPONENTS
C BETA IS THE ARRAY OF BETA ZEROS
C U IS THE ARRAY OF IONIZATION POTENTIALS
C COORD IS THE ARRAY OF CARTESIAN COORDINATES
C AW IS THE ARRAY OF ATOMIC WEIGHTS
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85 .

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C  THE FOLLOWING ARRAYS ARE READ IN ONCE AND ARE USED TO CONSTRUCT THE
C  ABOVE ARRAYS EACH TIME AN ATOM IS FED IN
C  SZ IS ARRAY OF CORE CHARGES
C  SZS IS THE ARRAY OF SLATER EXPONENTS
C  SBETA IS ARRAY OF BETA ZEROS
C  SUS US ARRAY OF IONIZATION POTENTIALS FOR S ORBITALS FOR CNDO/1
C     FIRST ROW IS FOR CNDO/1, SECOND ROW FOR CNDO/2
C  SUP IS IONIZATION POT. FOR P ORBITALS, FOLLOWING SUS CONVENTION
C  SAW IS ARRAY OF ATOMIC WEIGHTS
C  SUBROUTINE CONV CONVERTS BOND ANGLES AND DISTANCES INTO CARTESIAN COORD.
      IF(IFBF-12345) 10,20,10
   10 READ (50,100) (SZ(I), I = 1,9)
      READ (50,100) (SZS(I), I = 1,9)
      READ (50,100) (SBETA(I), I = 1,9)
      READ (50,100) (SUS(1,I), I = 1,9)
      READ (50,100) (SUP(1,I), I = 1,9)
      READ (50,100) (SUS(2,I), I = 1,9)
      READ (50,100) (SUP(2,I), I = 1,9)
      READ (50,100) (SAW(I), I = 1,9)
      WRITE (51,121)
      WRITE (51,101) (SZ(I), I = 1,9)
      WRITE (51,122)
      WRITE (51,101) (SZS(I), I = 1,9)
      WRITE (51,123)
      WRITE (51,101) (SBETA(I), I = 1,9)
      WRITE (51,124)
      WRITE (51,101) (SUS(1,I), I = 1,9)
      WRITE (51,125)
      WRITE (51,101) (SUP(1,I), I = 1,9)
      WRITE (51,126)
      WRITE (51,101) (SUS(2,I), I = 1,9)
      WRITE (51,127)
      WRITE (51,101) (SUP(2,I), I = 1,9)
      WRITE (51,128)
      WRITE (51,101) (SAW(I), I = 1,9)
      IFBF = 12345
```

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   20  CONTINUE
       READ (50,102)
       wRITE (51,102)
       READ (50,103), N, NH, NO, (IPT(I), I = 1,5)
       IF(N) 1000,1000,21
 1000  STOP
   21  CONTINUE
       DO 25 I = 1,N
   25  READ (50,114) (ISTP(I), NOAT(I), AL(I), TH(I), PH(I), BONDL(I))
       WRITE (51,129)
       DO 26 I = 1,N
   26  wRITE (51,130) (ISTP(I), NOAT(I), AL(I), TH(I), PH(I), BONDL(I))
       CALL CONV(N,ISTP,AL,TH,PH,BONDL,NOAT,ROX,IST,CE,COORD)
       NOT = N-NH
       NT = 4*NOT+NH
       DO 30 I = 1,N
       IN = NOAT(I)
       AW(I) = SAW(IN)
       Z(I) = SZ(IN)
   30  ZS(I) = SZS(IN)
       IW = IPT(4)
       DO 35 I = 1,NOT
       IM = 4*I-3 ,
       IN = NOAT(I)
       U(IM) = -SUS(IW,IN)
       BETA(IM) = -SBETA(IN)
       IM = IM+1
       IX = IM+2
       DO 35 J = IM,IX
       BETA(J) = -SBETA(IN)
   35  U(J) = -SUP(IW,IN)
       NS1 = 4*NOT+1
       DO 40 I = NS1,NT
       U(I) = -SUS(IW,1)
   40  BETA(I) = -SBETA(1)
       IF(IPT(1)+1) 45,50,45
```

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```
45    WRITE (51,104)
      WRITE (51,105) N,NH,NO, (IPT(I), I = 1,5)
      WRITE (51,106)
      WRITE (51,101)     (Z(I), I = 1,N)
      WRITE (51,108)
      WRITE (51,101)     (ZS(I), I = 1,N)
      WRITE (51,109)
      WRITE (51,101)     (BETA(I), I = 1,NT)
      WRITE (51,110)
      WRITE (51,101)     (U(I), I = 1,NT)
      WRITE (51,112)
      WRITE (51,113)     ((COORD(I,J), I = 1,3), J = 1,N)
50    DO 55 I = 1,NT
      BETA(I) = BETA(I)/27.21
55    U(I) = U(I)/27.21
      RETURN
100   FORMAT (9F5.3)
101   FORMAT (1H ,10F8.3)
102   FORMAT (80H
     1
103   FORMAT (8I2)
104   FORMAT (80H      NO. ATOMS          NO. H ATOMS         NO. OCCUPIED ORB
     1ITALS       BRANCH CODE      )
105   FORMAT (8X,12,17X,12,18X,12,15X,5I2)
106   FORMAT (16H CHARGES ON CORE)
108   FORMAT (17H SLATER EXPONENTS)
109   FORMAT (11H BETA ZEROS)
110   FORMAT (2H U)
112   FORMAT (12H COORDINATES)
113   FORMAT (1H ,5F12.6)
114   FORMAT (12,13,4F10.5)
121   FORMAT (22H TABLE OF CORE CHARGES)
122   FORMAT (26H TABLE OF SLATER EXPONENTS)
123   FORMAT (36H TABLE OF BETA ZEROS, NEGATIVE UNITS)
124   FORMAT (41H TABLE OF IONIZ. POT., S ORBITALS, CNDO/1)
125   FORMAT (41H TABLE OF IONIZ. POT., P ORBITALS, CNDO/1)
```

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```
126 FORMAT (39H TABLE OF 0.5*(I+A), S ORBITALS, CNDO/2)
127 FORMAT (39H TABLE OF 0.5*(I+A), P ORBITALS, CNDO/2)
128 FORMAT (23H TABLE OF ATOMIC MASSES)
129 FORMAT (67H   STP  AT.NO.   ALPHA        THETA           PHI
    1BOND LENGTH )
130 FORMAT (1H ,I3,3X,I3,4F14.6)
    END

C   SUBROUTINE CONV(N,ISTP,AL,TH,PH,BONDL,NOAT,ROX,IST,CE,CD)
C  THIS SUBROUTINE CONVERTS ARRAYS OF BOND ANGLES AND DISTANCES INTO
C  THE ARRAY CD, CARTESIAN COORDINATES.
C  DUMMY ATOMS, IDENTIFIED BY NOAT = AT. NO. = ZERO ARE REMOVED FROM THE
C   FINAL ARRAY.  HYDROGEN ATOMS, IDENTIFIED BY NOAT = 1 ARE PLACED AT
C   END OF ARRAY.
C  N IS THE NUMBER OF POSITIONS TO BE TRACED OVER
C  ISTP IS THE STARTING POINT BEFORE EACH TRACE
C  AL, TH, AND PH, CONTAIN THE ANGLES FOR ROTATIONS ABOUT Z, X, THEN Y AXIS
C   RESPECTIVELY
C  BONDL CONTAINS THE BOND LENGTHS
C  AW CONTAINS THE ATOMIC MASSES
C  ROX, CE, AND IST ARE WORKING SPACES
C  CD IS THE MATRIX OF COORDINATES DETERMINED BY THE PROGRAM
    DIMENSION ISTP(18), AL(18), TH(18), PH(18), BONDL(18), NOAT(18),
   1ROX(18,3,3), IST(18), CD(3,18), CE(3,18)
    DO 217 I = 1,N
    CA = COSF(0.017453293*AL(I))
    SA = SINF(0.017453293*AL(I))
    CT = COSF(0.017453293*TH(I))
    ST = SINF(0.017453293*TH(I))
    CP = COSF(0.017453293*PH(I))
    SP = SINF(0.017453293*PH(I))
    ROX(I,1,1) = CA*CP+SA*ST*SP
    ROX(I,1,2) = -SA*CP+CA*ST*SP
    ROX(I,1,3) = CT*SP
    ROX(I,2,1) = SA*CT
    ROX(I,2,2) = CA*CT
```

```
      ROX(I,2,3) = -ST
      ROX(I,3,1) = -CA*SP+SA*ST*CP
      ROX(I,3,2) = SA*SP+CA*ST*CP
  217 ROX(I,3,3) = CT*CP
      IA = 0
      IB = 0
  230 IF(IA-N) 235,4,4
  235 IA = IA+1
      IA1 = IA-1
      IF(IA1) 280,280,240
  240 IF(ISTP(IA)-IB) 245,245,270
C
C     BEGIN RETRACE TO PREVIOUS STARTING POINT
C
  245 ISTX = IST(IB)
      DO 260 I = 1,IA1
  260 CD(1,I) = CD(1,I)+BONDL(ISTX)
      DO 262 I = 1,3
      DO 262 J = 1,IA1
      CE(I,J) = 0.0
      DO 262 K = 1,3
  262 CE(I,J) = CE(I,J)+ROX(ISTX,K,I)*CD(K,J)
      DO 263 I = 1,3
      DO 263 J = 1,IA1
  263 CD(I,J) = CE(I,J)
      IB = IB-1
      IF(ISTP(IA)-IB) 245,245,270
C
C     ADDITION IF IA-TH ATOM
C
  270 DO 272 I = 1,3
      DO 272 J = 1,IA1
      CE(I,J) = 0.0
      DO 272 K = 1,3
  272 CE(I,J) = CE(I,J)+ROX(IA,I,K)*CD(K,J)
      DO 273 I = 1,3
```

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```
      DO 273 J = 1,IA1
273   CD(I,J) = CE(I,J)
      DO 275 I = 1,IA1
275   CD(1,I) = CD(1,I)-BONDL(IA)
280   DO 285 I = 1,3
285   CD(I,IA) = 0.0
      IB = IB+1
      IST(IB) = IA
      GO TO 230
C
C     REARRANGE ATOMS
C
4     NO = N
      DO 30 I = 1,N
      IF(NOAT(I)) 30,10,30
10    DO 20 J = I,N
      J1 = J+1
      NOAT(J) = NOAT(J1)
      DO 20 K = 1,3
20    CD(K,J) = CD(K,J1)
      NOAT(N) = 1
      NO = NO-1
      I=I 1
30    CONTINUE
      N = NO
C
C     ARRANGE HYDROGEN ATOMS LAST
C
      DO 50 I = 1,N
      IF(NOAT(I)-2) 40,40,50
40    I1 = I+1
      DO 42 J = I1,N
      IF(NOAT(J)-2) 42,42,43
42    CONTINUE
      GO TO 60
43    DO 44 K = 1,3
```

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```
 44 CE(K,1) = CD(K,J)
    ISN = NOAT(J)
    JS = J+1
    NO = J-I
    DO 45 K = 1,NO
    JS = JS-1
    JS1 = JS-1
    NOAT(JS) = NOAT(JS1)
    DO 45 L = 1,3
 45 CD(L,JS) = CD(L,JS1)
    DO 46 L = 1,3
 46 CD(L,I) = CE(L,1)
    NOAT(I) = ISN
 50 CONTINUE
 60 RETURN
    END
    END
    FINIS
-EXECUTE.
```

	1	2	3	4	5	6	7
12	65	975	15	1625	195	2275	26
9	9	13	17	21	25	31	39
1306	539	932	1405	1944	2558	3238	4020
	354	596	830	1067	1319	1585	1866
7176	3106	5946	9554	14051	16253	19032	2272
	1258	2563	4001	5572	7275	9111	11010
1	7	9	11	12	14	16	19

```
 1  ETHANE   STAGGER
10 6 7 0     215
 1  6
 2  1              120.0       110.86      1.102
 2  1                          110.86      1.102
 2  1              120.0       110.86      1.102
 2  6               60.0                   1.4660
 3  1               60.0       -69.14      1.102
 3  1              180.0       -69.14      1.102
```

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```
3  1    60.0        -69.14     1.102
2                              .775
3                   -90.
4  ETHANE (ECLIPSED)
10 6 7 1  250
1  6    120.0       111.28     1.102
2  1    120.0       111.28     1.102
2  1                111.28     1.102
2  6                           1.4633
3  1    60.00       -68.72     1.102
3  1    180.0       -68.72     1.102
3  1    60.00       -68.72     1.102
2                              .775
3                   -90.
```

APPENDIX

II   Computer output of Water (H_2O)
      (Sample calculation)

```
H20 OPTIMIIZE
STP AT.NO.  ALPHA        THETA      PHI      BOND LENGTH
 1   8      -0           -0         -0        -0
 2   1       52.110000   -0         -0         1.028900
 2   1      -52.110000   -0         -0         1.028900
 2  -0                   -0         -0        -0

   NO. ATOMS 3      NO. H ATOMS 2     NO. OCCUPIED ORBITALS 4    BRANCH CODE 1 0 0 250

CHARGES ON CORE
 6.000   1.000   1.000

SLATER EXPONENTS
 2.275   1.200   1.200

BETA ZEROS
-31.000  -31.000  -31.000  -31.000  -9.111  -9.111  -9.000  -9.000  -7.176  -7.176

U
-25.390  -9.111  -9.111  -9.111  -7.176  -7.176

COORDINATES
 0            0           0         0
.63189631   -.81199893   0         0
.63189631    .81199893   0         0

COORDINATES IN ATOMIC UNITS
 0            0           0         0
1.194134    -1.534485    0         .614147
1.194134     1.534485    0         .614147

DIRECTION COSINES
 0            0           0         .614147
-.614147     -.000000     0         .000000
-.614147     -.000000     0         .789191
 .789191     -.789191     0
-.789191     -1.000000    0         1.000000
 0            0           0
 0            0           0
 0            0           0

DISTANCES IN ATOMIC UNITS
 0            1.944377    1.944377   1.944377
1.944377     0           3.068970   3.068970
1.944377     3.068970    0
```

RHO

```
           0        3.378355    3.378355
    3.378355               0    3.682764
    3.378355        3.682764           0
```

TAU

```
           0         .309353     .309353
    -.309353               0           0
    -.309353               0           0
```

OVERLAP

```
    1.000000           0           0         .434263     .434263
           0    1.000000           0         .220063     .220063
           0           0    1.000000        -.282785     .282785
     .434263     .220063    -.282785     1.000000     .231503
     .434263     .220063     .282785      .231503    1.000000
```

GAMMA

```
     .826465     .476151     .476151
     .476151     .750000     .320779
     .476151     .320779     .750000
```

V

```
           0     .476151     .476151
    2.856904           0     .320779
    2.856904     .320779           0
```

F

```
    -.933113           0           0        -.319194    -.319194
           0    -.334840     .334840        -.161751    -.161751
           0     .334840    -.334840         .207853    -.207853
    -.319194    -.161751     .207853        -.263727    -.076572
    -.319194    -.161751    -.207853        -.076572    -.263727
```

ORBITAL ENERGIES
-1.442662 -.759905 -.701810 -.654866 .289195 .309628

C
```
  .880226    .051057       -0     .000000    .333614    .333614
  .000000   -.000000    .753527    .000000    .464864    .464864
 -.295445    .836979    .000000   -.000000    .325713    .325713
  .000000   -.000000    .000000  -1.000000    .000000    .000000
 -.371370   -.544848   -.000000    .000000    .531613    .531613
  .000000    .000000    .657417   -.000000    .532824    .532824
```

P
```
 1.724169   -.404680    .000000    .000000    .394850    .394850
 -.404680   1.406282    .000000       -0      .579297    .579297
  .000000    .000000   1.135605   -.000000    .700575    .700575
  .000000       -0     -.000000   2.000000    .000000       -0
  .394850    .579297    .700575    .000000    .866972    .002577
  .394850    .579297    .700575       -0      .002577    .866972
```

PA
```
 6.266056    .866972    .866972
```

F
```
-1.139160    .167227       -0        -0     -.413198   -.413198
  .167227   -.409526       -0         0     -.299668   -.299668
      -0        -0      -.297673   -.000000   -.374643   -.374643
      -0         0       .000000   -.654869    .000000       0
 -.413198   -.299668    .374643   -.000000   -.229602   -.076986
 -.413198   -.299668    .374643   -.000000   -.076986   -.229602
```

ENERGY
```
-17.570850   -.752501   -.752501
  -.412826    .010344
  -.412826
```
10 ITERATIONS
-19.89115807

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13. ABSTRACT

The approximate Self-Consistent Field Molecular Orbital Theory (ASCFT) with complete neglect of differential overlap (CNDO) has been applied to the calculation of electronic structure for several selected molecules in this text. The theory leads to calculated equilibrium geometry configurations and the barrier to internal rotation of ethane, inversion barrier of ammonia and the barrier for cis to trans conversion for difluorodiazine. These results are in reasonable agreement with experimental values in most cases. The stretching force constants are higher than experimental values by a factor of approximately two. The orbital energy levels for ammonia and for oxygen difluoride as a function of bond angles were in reasonable agreement with the full LCAO-SCF Calculations. A variation of parameters to find a new set of parameters was attempted with unsuccessful results.

The Extended Hückel Theory (EHT) can be applied to aliphatic hydrocarbons but its application to non-hydrocarbon molecules is quite limited.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Approximate Self-Consistent field theory						
Extended Huckel Molecular Orbital Theory						
Complete Neglect of Differential Overlap						
Barrier --						
NH_3 (inversion)						
C_2H_6 (eclipsed to stagger form)						
N_2F_2 (cis to trans)						
LCAO-SCF (Linear Combination of Atomic Orbital Self-Consistent Field)						
force constant						
equilibrium geometry (Bond length and Bond angle)						
ground singlet and doublet states						
Energy level diagram for						
F_2O						
NH_3						
J.A. Pople						
R. Hoffmann						

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